

**FORMATION, STRUCTURE AND PROPERTIES OF  
BORON NITRIDE FIBERS FROM POLYMER PRECURSORS**

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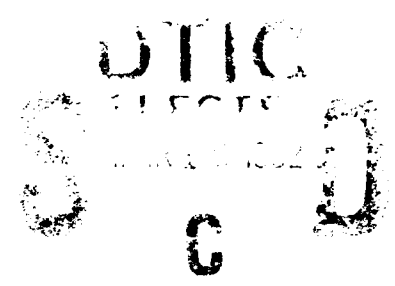
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**FINAL TECHNICAL REPORT**

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**School of Chemical Engineering**  
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# FORMATION, STRUCTURE AND PROPERTIES OF BORON NITRIDE FIBERS FROM POLYMER PRECURSORS

## I. INTRODUCTION AND OBJECTIVES

Recent advances in synthesis of precursor polymers which are suitable for conversion to desirable high performance refractory materials are among the most important developments in Materials Science and Engineering. A broad range of materials, covering a spectrum of physical and mechanical properties, is being developed to meet a variety of highly specialized needs [1-4]. These materials offer the potential for forming fibrous structures with unique combinations of properties such as high stiffness and strength, high temperature performance, unique electrical properties and interactions with electromagnetic radiation. Significant among these are precursors for fiber structures of materials such as boron nitride, which can offer the combination of high specific modulus and specific strength, high temperature (oxidation) resistance and optical transparency over a broad range of the electromagnetic spectrum. In spite of the important advances in the chemistry of precursor polymer materials for these ceramic structures [5-15], significant issues pertaining to continuous fiber formation and thermochemical conversion and consolidation remain to be resolved in developing a satisfactory process for the formation of boron nitride fibers. These are related to choice of precursor materials and precursor fiber formation route, and the effects of these fields and environments during fiber formation and its subsequent conversion to boron nitride. Among the main considerations in choosing the precursor material is the potential to produce it in large quantities and the "spinnability" of the fluids (melt or solution) that can be obtained from it.

The primary objectives of the research reported here have been to establish rational options for converting polymer precursors to high performance boron nitride fibers through a fundamental study, identifying the appropriate mutually dependent requirements in

(i) Precursor polymer selection: The requirement here is reproducible synthesis of precursor polymer with the potential for yielding fluids of spinnable rheological characteristics, which can be converted subsequently to a dense boron nitride structure.

(ii) Formation of precursor fibers: Identification of a continuous fiber formation process for the specific precursor material on hand.

(iii) Thermochemical consolidation: Thermal treatments of the precursor fibers in an appropriate environment for controlled chemical conversion and consolidation to yield dense boron nitride fibers.

The underlying theme of this study is to identify the "material-process-structure-property" interactions in the formation of continuous boron nitride fibers with high morphological order.

## II. SUMMARY OF PROCEDURES AND RESULTS

In this research, the rational options for synthesis and conversion of polymer precursors to high performance boron nitride fibers are being explored through a fundamental study of the mutually dependent requirements in precursor polymer synthesis, formation of continuous precursor fibers, and thermochemical conversion and consolidation to BN fibers. Preceramic fibers from the following polymers<sup>1</sup> have been investigated as precursors:

- (i) Unconsolidated polyborate sol-gel fibers from trimethoxyboroxine. The premise was that diffusion limitations which had existed in earlier studies during nitriding of boron oxide may be avoided here.
- (ii) Polyborazylene, a polyborazine of fused borazine polycyclic structures soluble in monoglyme or tetrahydrofuran. The polymer was obtained from Dr. Larry Sneddon, University of Pennsylvania. The polymer was synthesized by heating liquid borazine in vacuo at 70°C to produce the soluble polymeric product.
- (iii) Polymers from decaborane and  $(\text{Me})_2\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{Me})_2$ . The polymer was obtained from Dr. Seyferth of M.I.T.
- (iv) A polyborazine from B-triamino-N-tris (trimethylsilyl) borazine and a polyborazine from chloroborazine and hexamethyl disilazane which was investigated by Dr. Paciorek of Ultrasystems, Inc. The latter route, also researched by Dr. Paine of University of New Mexico, has been the subject of a number of publications. The latter polymer is also called poly(borazinyl amine).

Requirements of a candidate precursor material include reproducible synthesis of a spinnable precursor polymer, development of a continuous fiber

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<sup>1</sup>listed in the order of emphasis in the study reported here

formation process, and thermochemical conversion and consolidation to yield dense boron nitride fibers. The requirement that the precursor material for BN fibers should be amenable to being processed into an oriented morphology has to be included along with other criteria. Polyborazines, poly(vinyl borazine), poly(decaborane-diamine), poly(vinyl pentaborane) and polyborates are among the precursors being explored for this purpose in various laboratories [9, 14, 16-32]. BN fibers have been produced by nitriding melt-spun boron oxide at high temperatures (200-800°C) in an ammonia environment [33-38]. These fibers are, however, isotropic (as shown by wide angle x-ray diffraction) and lacking in mechanical properties, unless they can be drawn effectively at very high temperatures (~2000°C in nitrogen), which is difficult to accomplish in practice. The low diffusion rates of ammonia in the dense boron oxide precursor and the outer BN sheath that forms with nitridation also present the problem of long nitridation times to achieve close to full conversion to BN [35]. An alternative route that has been explored in this study consists of a porous polyborate precursor fiber which can be formed by "sol-gel" chemistry beginning with trimethoxyboroxine and boric acid [25] or disproportionation of trimethoxyboroxine alone.

Earlier paths to polyborates had consisted of routes which involved either the reaction of cyclohexanol with boric acid or boron oxide with the removal of water as an azeotrope with toluene or xylene [26, 27], or hydrolysis and polycondensation of boron alkoxides in the presence of alkali metal alkoxides whereby the metal becomes a counterion to the tetracoordinate boron in the polyborate structure [28-31]. It is possible to form polyborate gel fibers through these routes, as will be shown later (sections II.1.2-II.1.5). Presence of the metal counterion in the structure is, however, undesirable for conversion to BN. Concern over the presence of residual organics, such as toluene or xylene, which might lead to excessive residual carbon upon thermochemical conversion, or metal ions which may be difficult to remove from the polyborate precursors, has motivated the development of more direct routes. We have shown that it is possible to produce a spinnable polyborate sol without incorporating a counterion by a direct polycondensation of trimethoxyboroxine and boric acid or disproportionation of trimethoxyboroxine (section II.1.8). Spinnability of this sol can be improved significantly with a low concentration of a high molecular weight polymer as a rheological aid which is fugitive during thermochemical conversion.

Among the boron-nitrogen precursors which are currently being explored by several research groups as precursors for boron nitride, namely, polyborazines, poly(vinyl borazine), poly(vinyl pentaborane) and poly(decaborane-diamine) structures, only the unsubstituted polyborazine - polyborazylene - appears to offer a reasonable scheme for producing oriented BN through precursor orientation. It should be noted that all of these precursors for BN require almost prohibitively expensive starting materials.

In the following sections we present studies regarding formation of precursor polymers, characterization of the chemistry involved, formation of precursor fibers, and thermochemical conversion to boron nitride. Solution-based and low temperature melt-based fiber formation routes have been identified for the preparation of precursor fibers.

## II.1 OXIDE PRECURSORS FOR BORON NITRIDE

### II.1.1. Introduction

A method for the preparation of boron nitride fiber from melt spun boron oxide fiber was reported by Economy et al. as a result of research efforts at The Carborundum Company [33–38]. Boron nitride fibers were prepared by allowing the boron oxide precursor fibers to react with ammonia under conditions of controlled heating from room temperature to  $\sim 800^{\circ}\text{C}$ , followed by a final stabilization for  $\sim 5$  seconds under tension at  $\sim 2000^{\circ}\text{C}$  in a nitrogen atmosphere. A few fibers with a tensile strength of  $300 \times 10^3$  psi (2.0 GPa) and a tensile modulus of  $50 \times 10^6$  psi (350 GPa) were produced. On average, however, oriented BN fibers with a tensile strength of  $50 \times 10^3$  to  $125 \times 10^3$  psi (0.34 to 0.86 GPa) and tensile modulus of  $4 \times 10^6$  to  $12 \times 10^6$  psi (28 to 83 GPa) were produced. The process was hampered by the slow diffusion of ammonia into the melt spun boron oxide fiber, causing the heating schedule to last up to 14 hours in some cases. The overall BN yield for melt spun boron oxide fiber approached  $\sim 70\%$  [37].

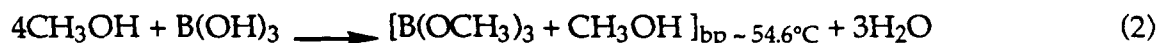
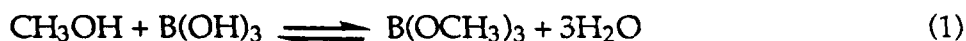
Oxide gel fibers obtained through the sol-gel process from viscous metal alkoxide solutions serve as precursors for oxide fibers [3]. In the case of precursors for BN fibers, the "less consolidated" structure of these fibers is expected to allow faster and more complete diffusion of  $\text{NH}_3$  into the fibers during nitridation. The problems which have been encountered in the conversion of boron oxide to BN at the core of the melt-spun boron oxide fibers may be eliminated. The alkoxide route would also offer the potential for the formation of mixed nitride fibers such as those of boron, silicon and titanium. It is also expected that the routes with oxide precursor fibers, if successful, would be more cost effective than those from polyborazines and melt spun boron oxide.

The current investigation involves studies related to molecular structure development as well as fiber formation in polyborate sol-gel systems. The former aspect involves understanding structure development on a molecular scale by suitable spectroscopic and allied techniques.



Various routes to polyborates have been reported in the literature. One of these routes involves the reaction of cyclohexanol with boric acid or boron oxide with removal of water as an azeotrope with toluene or xylene [26, 27]. Concern over the presence of residual organics, such as toluene or xylene which may lead to excessive carbon during thermochemical conversion, or alternatively tetracoordinate metal ions, which may be difficult to remove from polyborate precursors, has motivated the development of direct polycondensation of trimethoxyboroxine and boric acid to form a polyborate. Alternatively, it was found that disproportionation of trimethoxyboroxine above 130°C also leads to formation of polyborate [39].

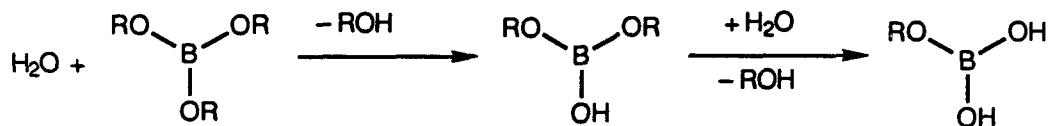
Unlike silicon alkoxides that hydrolyze relatively slowly and incompletely even in the presence of excess water, boron alkoxides hydrolyze rapidly resulting in precipitation of boric acid, making the usual hydrolysis and polycondensation route ineffective for the formation of polyborate gels [28]. Also, the preparation of trialkyl borates requires special consideration since they form azeotropes with their respective alcohols which are the lowest boiling constituents of their respective borate-alcohol systems [27]. For example, the trimethyl borate-methanol azeotrope at 54.6°C, 760 mm Hg has been reported [40] to contain molar ratios of ester to methanol of 0.949 to 0.967. For all practical purposes, the azeotrope is equimolar in ester and methanol and, therefore, the stoichiometry of Equation 1 for the esterification of boric acid is altered to that of Equation 2. Trimethyl borate alone boils at 68°C which is higher than the 54.6°C boiling temperature of the azeotrope. Water will react further to hydrolyze boron alkoxides present in solution unless it is removed.



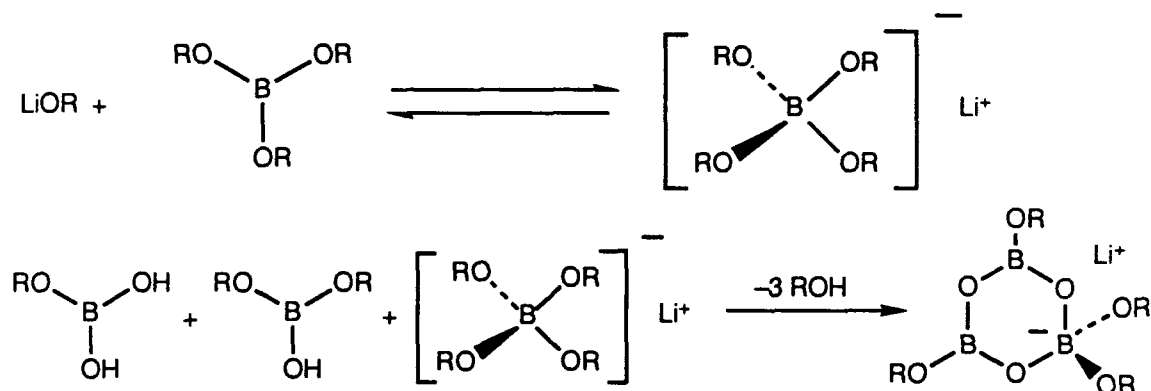
Studies by Weinberg et al. [28] and Brinker et al. [29, 30] have demonstrated the formation of borate gels by the reaction of trialkyl borates with lithium methoxide in a mixed alcohol and water solvent system. The postulates by Edwards and Ross [41] define the restrictive structural requirements for the formation and stability of hydrated polyborates. The ability to form a trimeric ring containing both tricoordinate and tetracoordinate borons and the stability of the tetracoordinate borons in a hydrolytic environment are important criteria for the formation of polyborate structures. An illustration of one of the mechanistic possibilities for the lithium polyborate sol-gel process involving a trialkyl borate is provided by Brinker in a simplified scheme (fig. 1, [29]). Condensation presumably occurs by the

nucleophilic attack of the alkoxy oxygen attached to tetracoordinate boron on the electrophilic tricoordinate boron carrying the hydroxyls formed by hydrolysis [29].

(i) Partial hydrolysis of borate precursor:



(ii) Condensation to form primary units:



(iii) Linkage of units to form polymer network:

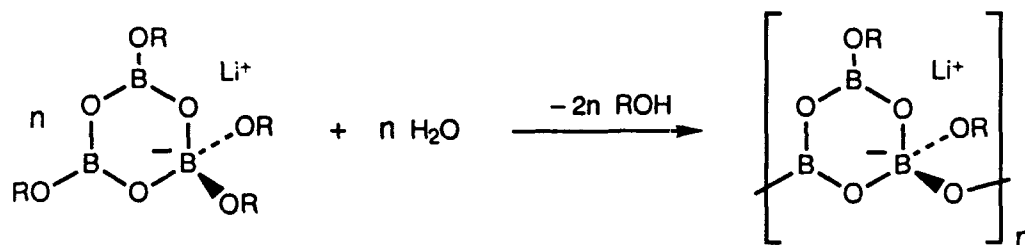


Fig. 1. Lithium polyborate sol-gel reaction from trialkyl borate (mechanism adapted from [29]).

An infinite series of polyborates can be envisaged without a metal counterion and with increasing ratios of boron to alkoxy, with the ultimate member being a single alkoxy buried in a boron oxide type matrix. A polyborate is, in essence, any alkoxyated boron oxide matrix intermediate in the series  $(\text{RO})_3\text{B} \dots (\text{ROBO})_6\text{B}_2\text{O}_3 \dots \text{B}_2\text{O}_3$  [27] (fig. 2).

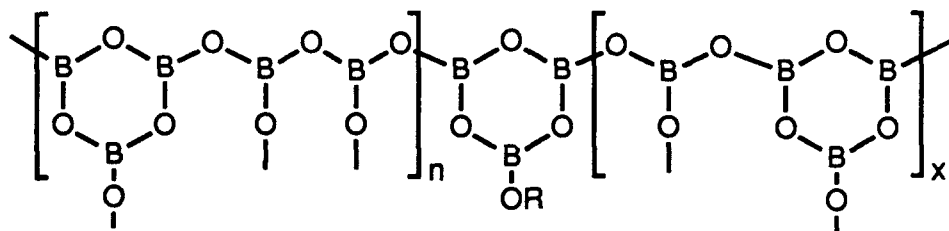


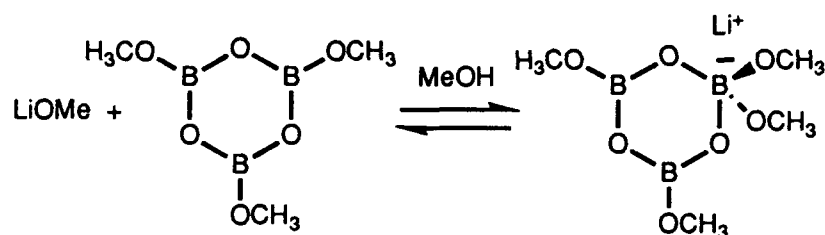
Fig. 2. Generalized polyborate structure.

High molecular weight organic polymers, such as poly(vinyl alcohol) and poly(ethylene oxide), have been used to control rheology and increase the spinnability of sol-gel derived precursors to ceramic oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3\text{-SiO}_2$  [42] and  $\text{ZrO}_2$  [43]. Spinnable polyborate precursors to boron nitride, formed with a low concentration of a high molecular weight polymer as a rheological aid which is fugitive during thermochemical conversion, have been demonstrated in this study. Poly(ethylene oxide) (PEO), poly(N-vinyl-2-pyrrolidinone) (PVP), and poly(methyl methacrylate) (PMMA) were found to be suitable for use in sol-gel reactions as polymeric processing additives.

In the present study, the lithium polyborate sol-gel process was initially investigated in detail using tri-n-butyl borate as well as trimethoxyboroxine (a six-membered cyclic boron alkoxide) as starting materials. The advantage of the metaborate is that it can directly form the primary structural unit with lithium alkoxide by complexation using ambient humidity to induce the hydrolysis and polycondensation reaction sequence (fig. 3), whereas tri-n-butyl borate would require controlled initial addition of water to the reaction mixture for partial hydrolysis leading to the formation of the cyclic trimer in a subsequent condensation step (fig. 1). The initial proportions of the reactants were chosen so as to obtain a gel-forming binary oxide composition [28, 29] that can be used as a model system to examine the concepts involved in polyborate formation. The transformations occurring during the consolidation of the lithium polyborate gels obtained from tri-n-butyl borate as well as trimethoxyboroxine have been studied using thermal analyses and x-ray diffraction. The sol-gel reaction of trimethoxyboroxine incorporating sodium as counterion has also been examined to infer the general applicability of this process. Synthesizing polyborates with ammonium counterion instead of an alkali metal counterion in the polyborate structure was attempted, since the former would be eliminated as ammonia, providing a metal-free boron oxide precursor for nitriding.

In the following we present pertinent examples of different approaches to synthesis, characterization, and fiber formation of polyborates.

(i) Complexation with LiOMe:



(ii) Hydrolysis-Polycondensation to form a polymer network:

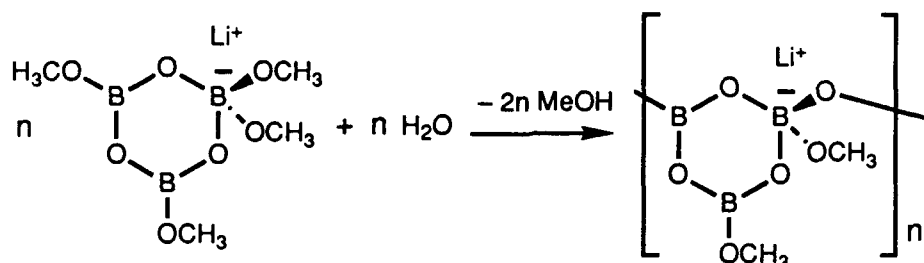


Fig. 3. A probable scheme for lithium polyborate sol-gel reaction from trimethoxyboroxine.

### II.1.2. Lithium polyborate from tri-n-butyl borate

The procedure employed was similar to the one reported by Weinberg et al. [28] for the formation of a binary oxide with the molar composition of 0.30  $\text{Li}_2\text{O}$ . 0.70  $\text{B}_2\text{O}_3$ . Lithium methoxide (0.066 mole) was dissolved in methanol (0.616 mole) and freshly distilled water (0.140 mole). Tri-n-butyl borate (0.154 moles) was added dropwise to the above solution. After mixing at room temperature, the clear sol was aged at 50°C in a 95% relative humidity environment. Fibers could be drawn from the viscous, translucent sol after 12 hours (Sol 1). The drawn fibers were air dried at room temperature to produce dried fibers. A part of the sol was dried at 90°C in vacuum for 12 hours to obtain a white powder. When a sol of the same initial composition was aged at room temperature in 100% relative humidity (Sol 2), gelation occurred in 18 hours.

$^{11}\text{B}$  NMR studies are useful for identifying tricoordinate and tetracoordinate boron environments [44] in the polyborate structures generated by the sol-gel process. A 50% solution of the viscous, fiber-forming Sol 1 in 1-methyl-2-pyrrolidinone (NMP) showed the presence of tricoordinate borons at a resonance of 18.5 ppm and a high field resonance at 1.8 ppm due to tetracoordinate borons in the borate structure [25]. The resonance at 2.9 ppm presumably arises due to the coordination of the amide solvent with the tricoordinate borons in the polyborate

structure creating an additional tetracoordinate boron environment in the sol. An independent  $^{11}\text{B}$  NMR study of the lithium polyborate Sol 2, obtained by aging for 6 hours at room temperature, demonstrated that the fraction of the tetracoordinate borons in the borate sol is increased (as inferred from the appearance of the new boron resonance at 2.9 ppm) when NMP is added to the sol. This was also confirmed by additional  $^{11}\text{B}$  NMR experiments with 50 vol% solutions of trimethoxyboroxine in NMP and dimethylformamide (DMF) which revealed the presence of tetracoordinate boron resonances, although much lower in intensity, at 2.3 ppm and 3.7 ppm respectively, besides the major resonance at 18.5 ppm for the tricoordinate borons in trimethoxyboroxine.

An estimate of the ratios of the tricoordinate and tetracoordinate borons can be obtained from the integrated intensities of the resonances in the  $^{11}\text{B}$  NMR spectra. These indicate that there are borate structural units other than the cyclic trimer also present in the sol-gel derived polyborates. The  $^{11}\text{B}$  NMR studies can differentiate between tricoordinate and tetracoordinate borons but show no direct evidence for cyclic or linear structures in the polyborate. However, the presence of boroxine ring structures has been identified for polyborate ions in solution by Raman spectroscopy [45], and comparisons have also been made in the literature with the known structures for hydrated borates from x-ray diffraction [45].

Microstructural examination of the sol-gel derived fiber samples by scanning electron microscopy show that both the cross-section and the surface of the fiber from Sol 1 are highly porous (figs. 4 and 5) [25].

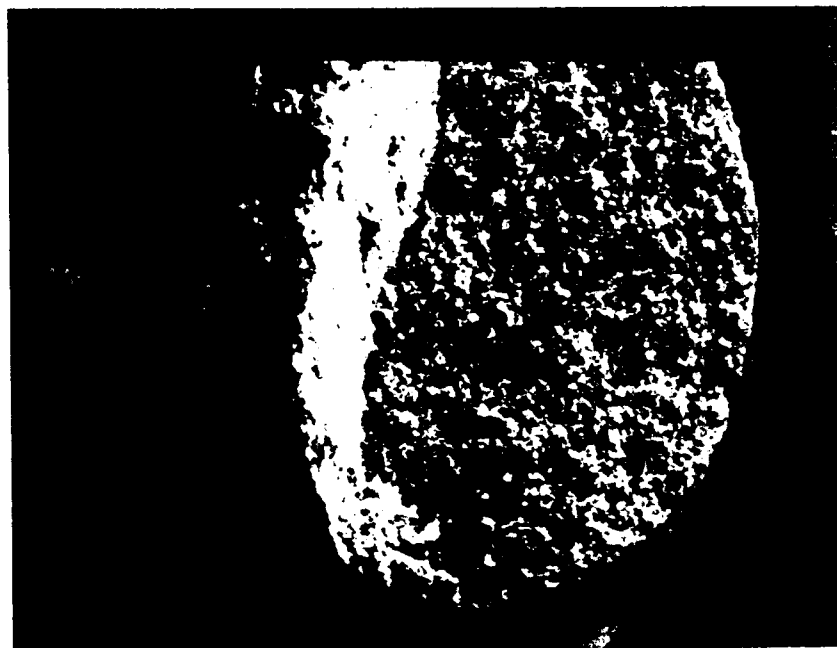


Fig. 4. SEM of the cross-section of lithium polyborate fiber from Sol 1 [25].



Fig. 5. SEM of the surface of lithium polyborate fiber from Sol 1 [25].

### II.1.3. Lithium polyborate from trimethoxyboroxine

A nearly 1:1 molar ratio of trimethoxyboroxine and lithium methoxide was used for the reaction. Trimethoxyboroxine (0.090 mole) was added dropwise to lithium methoxide (0.085 mole) in methanol (0.790 mole) and the mixture was aged in 100% relative humidity at room temperature (Sol 3). Fibers could be drawn from the transparent sol prior to gel formation that occurred in 20 hours. The drawn fibers were air dried at room temperature to obtain dried fibers. A part of the sol was also dried in vacuum at 90°C to obtain dried powder.

As indicated in figure 3, complexation of trimethoxyboroxine with LiOMe followed by hydrolysis and polycondensation in a humid atmosphere provides a plausible route for the formation of a polyborate structure. In the  $^{11}\text{B}$  NMR spectrum of Sol 3 (aged for 3 hours, no added solvent), the tetracoordinate boron appears at 1.8 ppm and the tricoordinate boron appears as a broad resonance centered at 12.8 ppm [25]. In the corresponding  $^7\text{Li}$  NMR spectrum, the dominant resonance (besides that of the external reference at 0.70 ppm due to LiBr) is that of the lithium counterion in the tetracoordinate borate environment at -0.13 ppm. The  $^{11}\text{B}$  NMR of the sol before aging (initial sol) shows the presence of tetracoordinate borons at 1.9 ppm and the tricoordinate borons at 13.6 ppm. The counterion in the tetracoordinate borate anion complex appears as the major resonance at -0.10 ppm in the  $^7\text{Li}$  spectrum. There was no LiOH resonance observed in these sols. Since no water was initially added in the sol-gel reaction, LiOMe and trimethoxyboroxine appear to have reacted in a 1:1 molar ratio, in the formation of the initial complex (fig. 3). However, the simplified scheme for lithium polyborate formation from trimethoxyboroxine (fig. 3) does not take into consideration reactions such as

methanolysis of trimethoxyboroxine [27] which would explain the formation of some boric acid (confirmed by IR) that was deposited on the walls of the container during the aging process.

The IR (KBr pellet) spectra of the air dried borate fiber drawn from Sol 1 and the dried gel from trimethoxyboroxine (Sol 3) show identical features. The tricoordinate B-O stretch occurs at  $1354\text{ cm}^{-1}$  and the other dominant bands are attributed to the tetracoordinate borate stretch at  $1028\text{ cm}^{-1}$  and the O-H stretch at  $3434\text{ cm}^{-1}$  [28]. The weaker bands in the spectra occur around  $1630\text{ cm}^{-1}$  (assigned to the deformation mode for the hydroxyl group [28]) and as a shoulder at  $895\text{ cm}^{-1}$ . In these spectra, no C-H absorption due to the alkoxy groups is observed indicating that the dried gels may have fully hydrolysed and partially condensed polyborate structures.

#### **II.1.4. Lithium polyborate from trimethoxyboroxine in presence of a rheological aid**

0.24 g of poly(N-vinyl pyrrolidinone), 2 wt% relative to the weight of trimethoxyboroxine (11.95 g, 0.068 mole) was dissolved in a solution of lithium methoxide (0.068 mole) in excess methanol (0.740 mole). Trimethoxyboroxine was added dropwise to the above solution which was aged at 100% relative humidity at room temperature. A viscous sol was obtained after 30 hours of aging. Long fibers could be drawn from the sol using a glass rod.

#### **II.1.5. Sodium polyborate from trimethoxyboroxine**

Polyborate incorporating sodium ion was synthesized by aging a reaction mixture of trimethoxyboroxine (0.055 mole) and sodium methoxide (0.053 mole) in methanol (0.469 mole) at room temperature in a 100% relative humidity atmosphere. Gelation occurred in 20 hours. The sol was dried as described earlier. The dried sodium polyborate gel has an IR spectrum indistinguishable from those of the lithium polyborates.

#### **II.1.6. Attempted ammonium polyborate sol-gel reaction**

Synthesis of spinnable sol-gel derived polyborates with ammonium counterion would be relevant in the context of providing a cation that can be removed during heat treatment as ammonia, resulting in the formation of a metal ion-free boron oxide precursor for chemical conversion to boron nitride fibers. 10 ml aqueous ammonium hydroxide (0.148 mole) was mixed in excess THF (0.90 mole) and the mixture was added dropwise to trimethoxyboroxine (0.148 mole). This resulted in instantaneous formation of a precipitate that was filtered and dried. The

reaction between trimethoxyboroxine and aqueous ammonium hydroxide appeared to result in the formation of a trimethyl borate-ammonia adduct. The same adduct was also obtained by bubbling ammonia gas into trimethyl borate [46, 47] in another experiment. This was also inferred from the identical IR spectra obtained for the products isolated from the two reactions.

Synthesis of ammonium polyborate was also attempted by a metal-ammonium counterion exchange between a sodium polyborate sol obtained from trimethoxyboroxine and ammonium bromide or ammonium iodide. Solubility related problems and a lack of evidence for exchange by a  $^{23}\text{Na}$  NMR experiments made these preliminary studies inconclusive.

#### II.1.7. Partial hydrolysis and polycondensation of trimethoxyboroxine

The formation of a polyborate in the *absence* of a counterion was investigated by addition of water (0.086 mole) in 100 ml THF to trimethoxyboroxine (0.172 mole). A viscous sol was found to result after solvent removal at 60°C in partial vacuum. However, the sol exhibited poor spinnability, apparently due to insufficient molecular weight. The same experiment was carried out with the inclusion of 0.5 gram (1.6 wt% relative to trimethoxyboroxine) of high molecular weight poly(ethylene oxide) as a polymer additive in the initial reaction mixture. Long fibers could be hand-drawn from the viscous sol with a glass rod.

Exploratory experiments in the partial hydrolysis and polycondensation of trimethoxyboroxine resulted in the formation of a viscous polyborate sol without the requirement of a counterion. The spinnability of the sol was greatly enhanced by incorporating poly(ethylene oxide) as a polymer processing aid. The IR spectrum of the viscous sol taken using AgCl plates shows a reduction in C-O stretch at 1080  $\text{cm}^{-1}$  relative to the reactant trimethoxyboroxine indicating partial hydrolysis. The IR also distinctly indicates the presence of the hydroxyl group at 3421  $\text{cm}^{-1}$  as well as that of the unreacted methoxy C-H bands at 2970  $\text{cm}^{-1}$ , 2881  $\text{cm}^{-1}$  and 1486  $\text{cm}^{-1}$ . The B-O stretch of the boroxine ring is observed in the sol in the region 1300-1400  $\text{cm}^{-1}$  and the ring deformation at 721  $\text{cm}^{-1}$  [48], indicating that the polyborate from the controlled hydrolysis process has a boroxine ring structural component.

#### II.1.8. Polycondensation and disproportionation of trimethoxyboroxine

Exploratory experiments were performed to study if it was possible to conduct solventless polycondensation of trimethoxyboroxine and boric acid without the requirement of a counterion. 40 ml trimethoxyboroxine (0.2755 mole) was added by gas-tight syringe transfer to 6.021 g boric acid (0.0974 mole), 2.83:1.00 mole ratio, and



1.000 g poly(ethylene oxide) (PEO,  $M_w = 100,000$ ). A 100 ml reaction flask with teflon boiling chips and a 100 ml receiving flask were used on a high boiling distilling apparatus. The reaction flask was immersed in an oil bath. Boiling began after the slurry was heated to 115°C under a slight vacuum (630 to 660 mm Hg). By heating to 120–125°C, a solution was obtained and a distillate started to collect. The temperature of the vapor in the distillation column was 47°C. To maintain distillation, the bath temperature was increased gradually to 150°C over 50 minutes. 10.4 ml of distillate was generated in the process. A translucent, light yellow, viscous product solution (Sol X, 2.2 wt% PEO) was obtained after cooling to room temperature.

In another experiment, 40 ml trimethoxyboroxine (0.2755 mole) was added by gas-tight syringe transfer to 6.021 g boric acid (0.0974 mole), 2.83:1.00 mole ratio, and 1.000 g poly(N-vinylpyrrolidinone) (PVP,  $M_w = 360,000$ ). A 100 ml reaction flask with teflon boiling chips and a 100 ml receiving flask were used on a high boiling distilling apparatus. The reaction flask was immersed in an oil bath. Boiling began after the slurry was heated to 115°C under a slight vacuum (630 to 660 mm Hg). By heating to 120–125°C, a solution was obtained and distillate started to collect. The temperature of the vapor in the distillation column was 47°C. To maintain distillation, the bath temperature was increased gradually to 175°C over 40 minutes. 15.2 ml of distillate was generated in the process. The product was a deep yellow, viscous solution at 175°C that, on cooling to room temperature, hardened to a tan solid.

These exploratory experiments demonstrated solventless polycondensation of trimethoxyboroxine and boric acid without the requirement of a counterion. They also demonstrated compatibility of high molecular weight poly(N-vinyl-2-pyrrolidinone) as a rheological aid for polyborate [49, 50]. These experiments were scaled up to a basis of 200 ml of trimethoxyboroxine with added stoichiometries of boric acid ranging from a 2:1 mole ratio of trimethoxyboroxine to boric acid to disproportionation of trimethoxyboroxine with no boric acid. The disproportionation of alkoxyboroxines has been reported [51]. A 500 ml reaction flask with teflon boiling chips and a 250 ml receiving flask were used on a high boiling distilling apparatus. The reaction flask was immersed in an oil bath. Boiling began after the slurry was heated to 110–130° (higher temperatures with less boric acid) under a slight vacuum (630 to 660 mm Hg). By heating to 120–125°C, a solution was obtained and a distillate started to collect. The temperature of the vapor in the distillation column ranged from 47–58°C (higher temperatures with less boric acid). To maintain distillation, the bath temperature was increased gradually to 265°C over about 2 hours. In the 2:1 and 4:1 syntheses boric acid was found to sublime out of the reaction flask after initially going into solution. Much more boric acid sublimed to the distillation column in the 2:1 reaction. In all cases, at 265°C the polyborate product began to foam so the reaction was stopped by cooling to room temperature.

A summary of the distillate amount and composition collected is shown in Table 1. The table reports analyses by  $^{13}\text{C}$  NMR of the mole% of methanol in the trimethyl borate and methanol distillates. All products were translucent, light yellow, and very viscous solutions which cooled to solids at room temperature.

**Table 1.** The composition of trimethyl borate – methanol distillates from polyborate synthesis as determined by  $^{13}\text{C}$  NMR<sup>1</sup>.

$(\text{CH}_3\text{OBO})_3 : \text{B}(\text{OH})_3$	Predicted <sup>2</sup>	Experiment	Experiment, 1 wt% PVP
2:1	47.8 mole% $\text{CH}_3\text{OH}$	39.6 mole% $\text{CH}_3\text{OH}$	35.2 mole% $\text{CH}_3\text{OH}$
3:1	47.8	—	35.5
4:1	47.8	34.7	32.7
6:1	39.0	—	19.6
10:1	26.1	21.1	15.7
1:0	0.0	0.0	PVP not soluble

<sup>1</sup> The initial trimethoxyboroxine contained 6.6 mole% trimethyl borate.

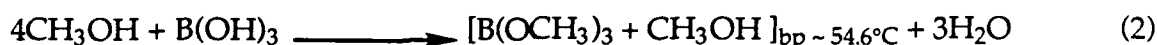
<sup>2</sup> It was assumed that condensation was completed prior to disproportionation.

Table 1 also summarizes the various syntheses carried out on the same scale as above, except that in each case 2.00 grams of poly(N-vinyl-2-pyrrolidinone) (PVP) with an average molecular weight of 1 million was added to the initial reactants. This represents approximately a final 1 wt% concentration of PVP in the polyborate products. Consistent with previous reactions, boric acid appeared to be in excess in 2:1, 3:1, and 4:1 reactions. Much less sublimed out of solution in the 4:1 reaction, more in the 3:1, and even more in the 2:1 reaction. The reactions were each carried out to a final temperature of 225°C. At this temperature the products began to foam. PVP was soluble at about 130°C in all reactions, except the disproportionation reaction where there was no boric acid present in the initial composition. The final products of each reaction were deep yellow melts at 225°C which then hardened to solids with varying shades of an opaque tan to translucent yellow. Initial compositions with less boric acid were more tan and opaque.

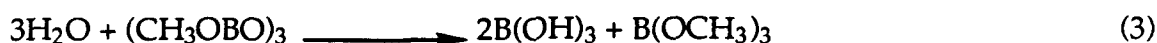
The mole ratio of trimethoxyboroxine to boric acid was purposely not in an initial 1:1 mole ratio as might be expected to balance condensation of two trifunctional species.  $^{13}\text{C}$  NMR of distillate from previous experiments showed that polycondensation of an initial 1:1 mole ratio of trimethoxyboroxine to boric acid resulted in a nearly 1:1 mole ratio of trimethyl borate and methanol in the distillate.

A trimethyl borate - methanol azeotrope of nearly 1:1 proportions at 54.6°C, 760 mm Hg has been reported [40]. This azeotrope is known to be formed by the reaction of methanol and boric acid (Equation 2) [27]. It was estimated that due to azeotrope formation and concurrent hydrolysis of trimethoxyboroxine (Equation 3), the polycondensation must be started at about a 2:1 or a larger ratio of trimethoxyboroxine to boric acid. Based on the observation that boric acid appears to be in excess with stoichiometries 2:1 and 3:1, a balanced reaction for condensation of trimethoxyboroxine and boric acid is proposed for the complete conversion to boron oxide in Equation 4. Equation 5 reports the disproportionation reaction by Steinberg [27]. From the  $^{13}\text{C}$  NMR analysis of the distillates, reported in Table 1, it is inferred that both condensation and disproportionation reactions occur simultaneously above 130°C when boric acid is present in the reaction mixture. This would explain the lower than predicted mole% of methanol in the trimethyl borate and methanol containing distillates.

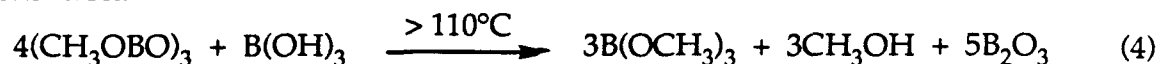
Azeotrope Formation:



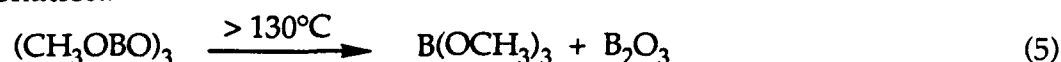
Hydrolysis:



Condensation:



Disproportionation:



The infrared spectra of the polyborates produced show a blending of the spectral features of trimethoxyboroxine and of boric acid (Fig. 6) [48, 52]. A decrease in the C-O stretch at  $1080\text{ cm}^{-1}$  and the retention of the ring deformation at  $720\text{ cm}^{-1}$  are representative of the proposed polyborate structure (Fig. 2). As indicated by the C-H stretch bands,  $2950$  and  $2880\text{ cm}^{-1}$ , and the hydroxyl stretch band at  $3200\text{ cm}^{-1}$ , methoxy and hydroxyl groups remain in all the polyborate products.

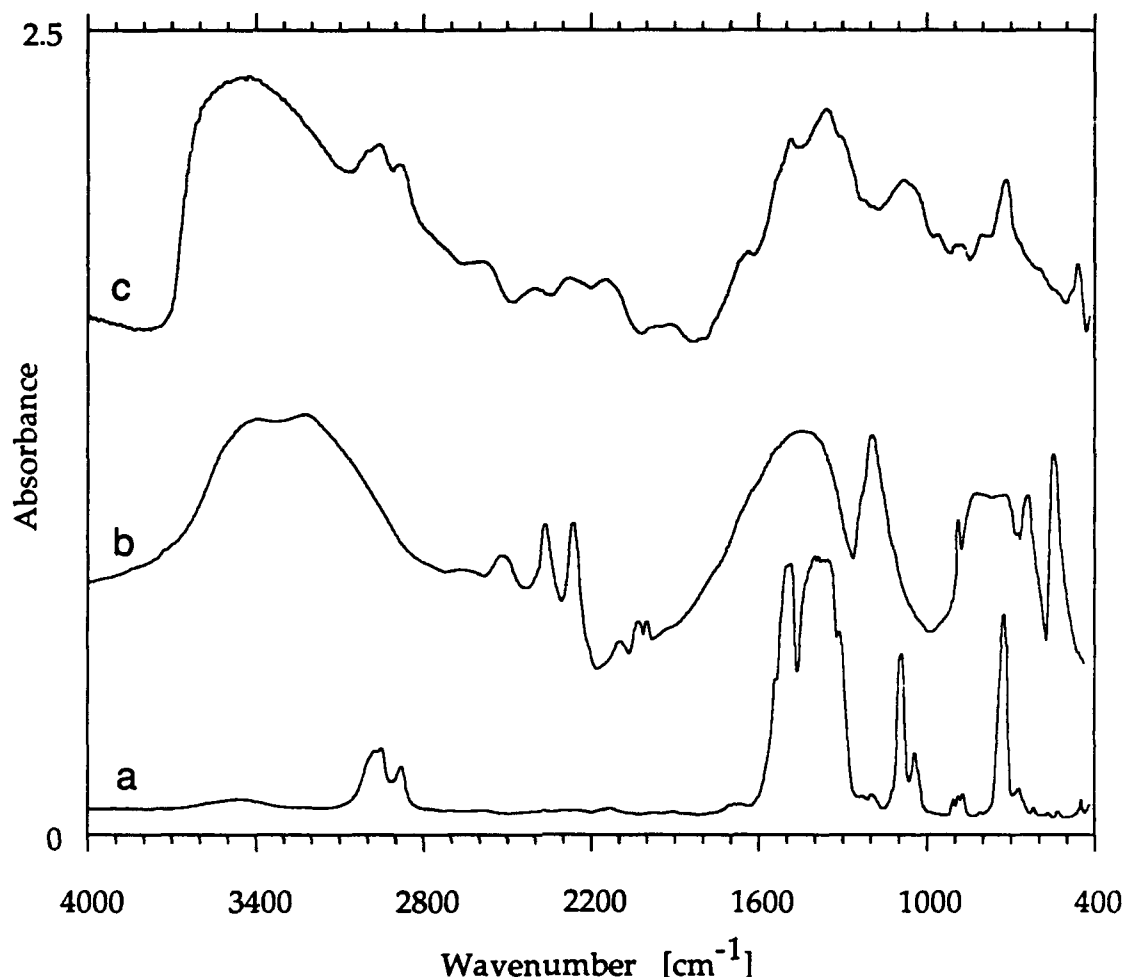


Fig. 6. Infrared spectra of a) trimethoxyboroxine, b) boric acid, and c) Sol 1.

A comparison of the distillate compositions of syntheses done with and without PVP shows a reduction in the mole% methanol when PVP was present in the initial composition. It was also found that PVP was not soluble when trimethoxyboroxine was disproportionated without added boric acid, thus not producing methanol. Methanol alone is a good solvent for PVP. PVP appears to require methanol for compatibility in polyborate. Analysis of the PVP removed from the disproportionation synthesis in which it was not soluble showed that it had become a cross-linked gel. Other candidate polymers to use as a rheological aid include poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc). They have been found to be completely soluble with trimethoxyboroxine and therefore either polymer can be directly used in the disproportionation synthesis to polyborate. PVAc, however, is not expected to be completely fugitive during

thermochemical conversion. It leaves a 25 wt. % carbonaceous residue on heating to 400°C in air. PMMA is completely lost under the same conditions.

Products from some of the polyborate syntheses were poured directly into a small scale melt spinning apparatus (Fig. 7) before they cooled. Since the polyborate products can be re-melted and solidified, the requisite viscosity for fiber spinning can be attained by heating, and the rigidity necessary for maintenance of fiber shape can be attained by cooling. 200 psi nitrogen pressure was typically used to extrude a polyborate product at ~135°C through a ten hole spinneret (63.5µm diameter spinneret holes). A 2µm Cajon filter was used in the spinning apparatus to prevent clogging of the spinneret. Fibers were stored on a bobbin in a large dessicator to prevent hydrolysis prior to thermochemical conversion. Fibers from polyborate with a rheological aid such as PVP or PMMA were found to be much more hydrolytically stable than those without an added polymer.

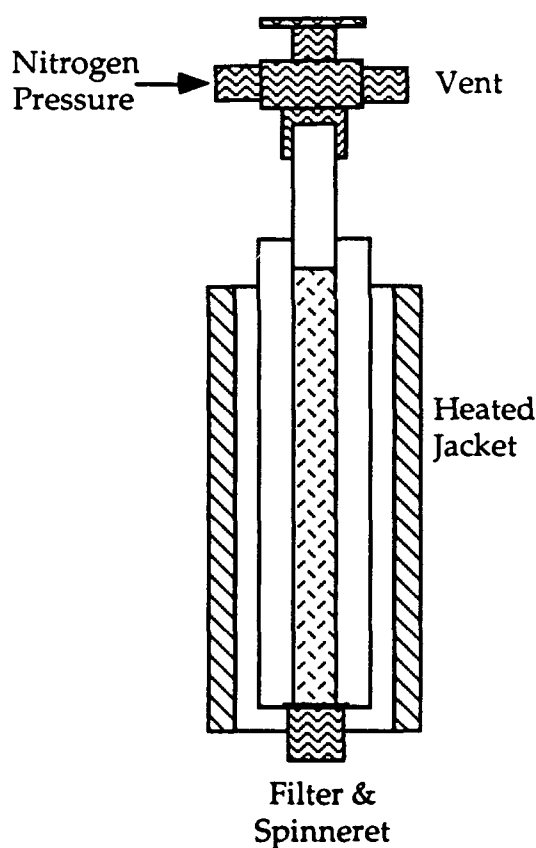


Fig. 7. Schematic of experimental apparatus used for melt spinning.

Polyborate samples were batch nitrided in an ammonia atmosphere at a heating rate of 1°C/min to 200, 300, 500, and 700°C. Infrared spectra of the samples

indicate that there is a loss of hydroxyls by 200°C and evidence of a partially nitrated structure (fig. 8). Infrared spectra for samples exposed to higher nitrating temperatures show increased absorbances for the N-H stretch at 3430  $\text{cm}^{-1}$ , the B-N stretch at 1350  $\text{cm}^{-1}$ , and the B-N-B bending at  $\sim 800$   $\text{cm}^{-1}$ . The grey color of the 700°C nitrated sample and the presence of an 1100  $\text{cm}^{-1}$  band is indicative of the B-C asymmetric stretch of some boron carbide present [53]. The boron carbide is expected to be removed with further nitrating. Boron oxide is still present in the sample nitrated to 700°C as indicated by the B-O stretch at  $\sim 1440$   $\text{cm}^{-1}$  and the  $(\text{BO})_3$  ring deformation at  $\sim 720$   $\text{cm}^{-1}$  [17, 54]. Also, a shoulder seen at  $\sim 1300$   $\text{cm}^{-1}$  on the B-N stretch absorbance region (1380–1360  $\text{cm}^{-1}$ ) is due to the  $(\text{BO})_3$  ring stretch. X-ray diffraction patterns (fig. 9) show the development of a turbostratic-like boron nitride pattern in the 700°C nitrated sample from the initially amorphous polyborate [55].

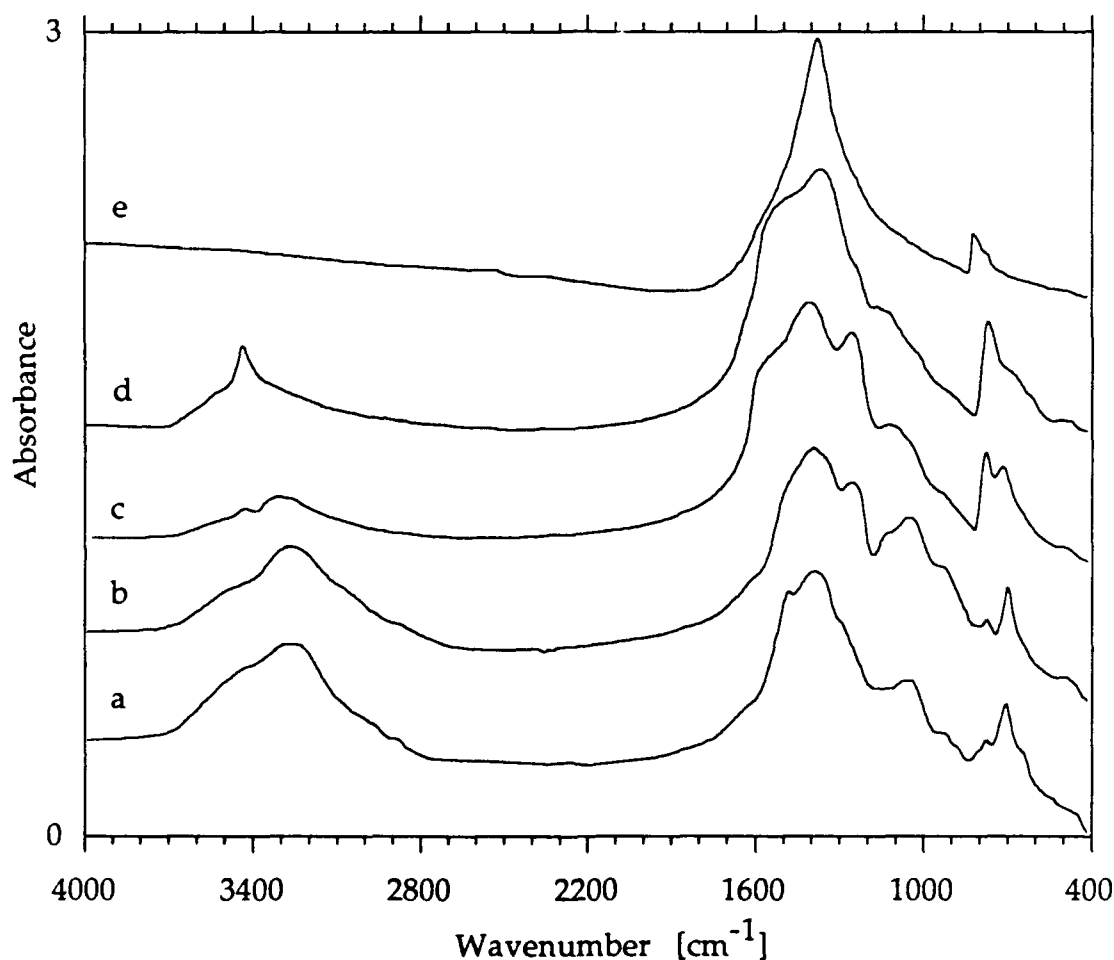


Fig. 8. Infrared spectra of Sol 1 nitrated to a) 200°C, b) 300°C, c) 500°C, and d) 700°C. e) Reference BN (Aldrich Chemical Company).

The  $T_m$  of polyborate increases during thermochemical conversion with further removal of trimethyl borate and methanol from the polyborate (only trimethyl borate in the polyborate from disproportionation). Loss of volatiles induces microporosity. A favorable implication of thermoplasticity is that the fibers can be deformed during thermochemical conversion in ammonia to densify them and hopefully yield an oriented boron nitride morphology.

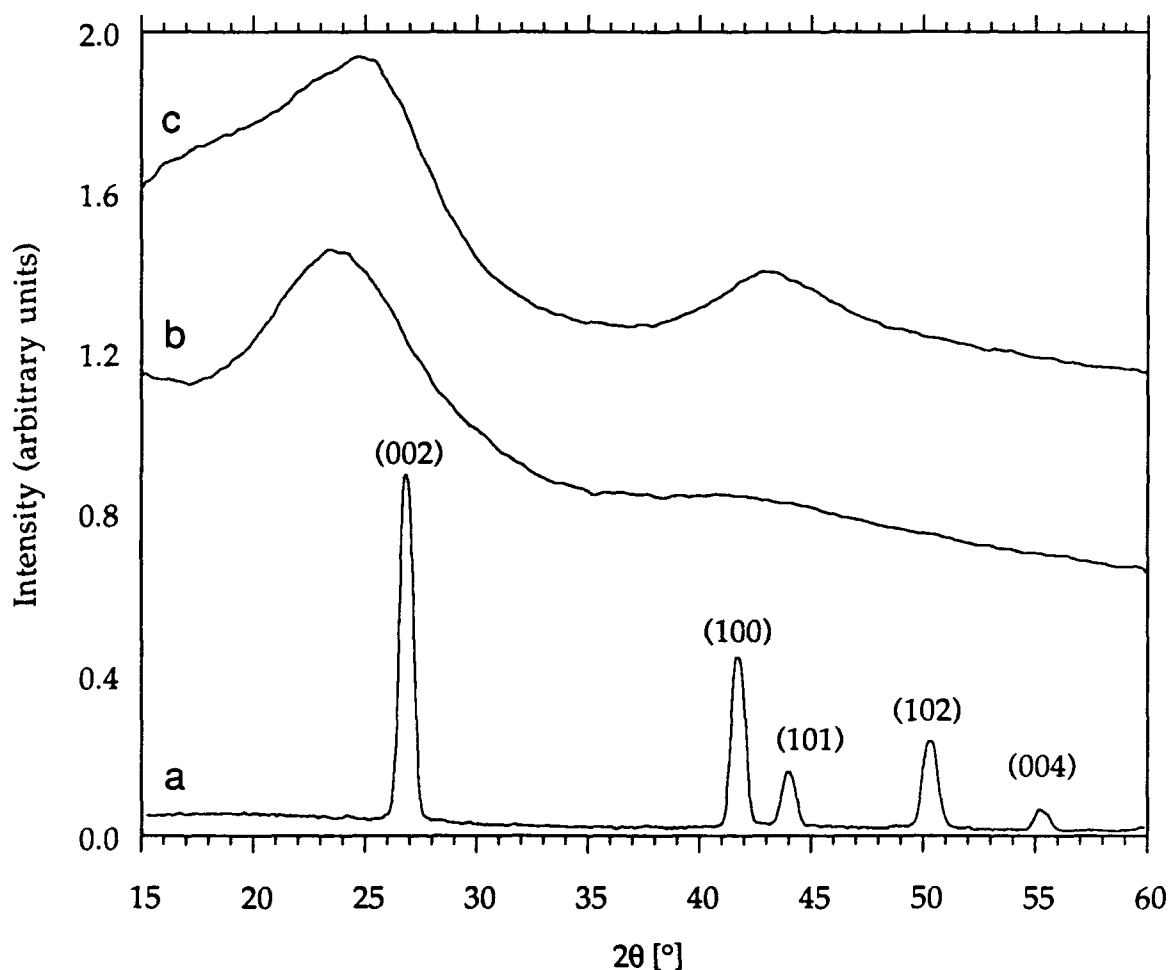


Fig. 9. X-ray diffraction patterns of a) hexagonal BN (Aldrich Chemical Company), b) Sol 1 (amorphous), and c) Sol 1 after nitriding to 700°C (turbostratic).

## II.2 NON-OXIDE PRECURSORS FOR BORON NITRIDE

### II.2.1. Introduction

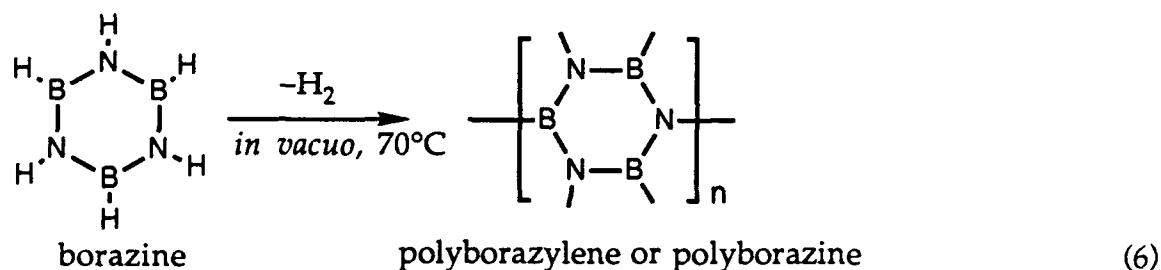
A number of examples of polyborazines have been reported. It appears that formation of six-membered boron-nitrogen ring compounds known as borazines is highly favored. As with the polyborate structure, the ring will crosslink unless functionalized with non-reactive groups. The corresponding polymers consist of borazine rings directly linked together by either  $=B-B=$  or  $=B-N=$  bonds [56]. Polyborazines in which a nitrogen atom of one borazine ring is linked to a nitrogen atom of a second borazine nucleus are unknown. Poly(borazinyl amines) which consist of borazine rings linked through borons of adjacent rings by  $-N(H)-$  or  $-N(R)-$  groups have been synthesized [9, 10, 12, 13, 19-21, 57-59]. Poly(borazinyl oxides) have been reported in which the borazine rings are linked by oxygen [60]. Borazines linked by sulfur, poly(borazinyl sulphides), are also known [19]. However, due to the large relative weight of the sulfur unit, a large weight loss on pyrolysis to boron nitride is found. Recently, the ability to synthesize B-vinyl borazine has allowed the synthesis of poly(vinyl borazine) [17, 54].

In general, the chemical properties of borazines appear to be more influenced by the polar nature of the B-N  $\sigma$ -bonding framework than by the aromaticity that arises as a result of  $\pi$ -electron delocalization [61]. This is illustrated by the addition of Lewis acids to ring nitrogen atoms and Lewis bases to boron atoms, and by the addition of very polar compounds across the B-N bond, the negative constituent adding to the boron and the positive one to the nitrogen. Hydrolytic and thermal instability is a major problem in borazine monomers and polymers, although this is very much reduced by the introduction of bulky carbon containing groups, which presumably offer steric protection to the ring. Polyborazines with bulky carbon containing side groups, however, present the problem of carbon retention on complete pyrolysis to boron nitride.

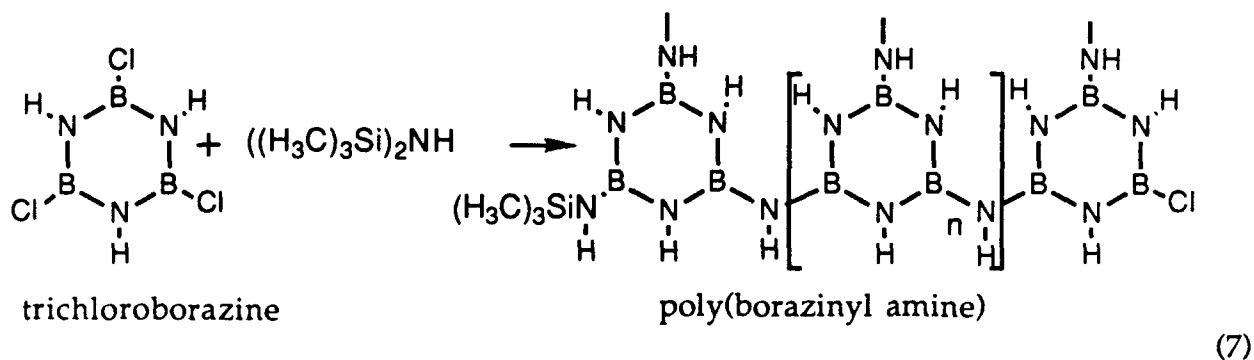
One of the most promising polyborazine precursors to boron nitride is polyborazylene. It is produced by thermally induced borazine dehydropolymerization. Small dehydrodimers (analogous to naphthalene and biphenyl) and oligomers of borazine have previously been prepared by pyrolytic dehydrogenation by heating between 340 and 440°C [62]. However, heating liquid borazine for ~48 hours in vacuo at 70°C results in a dehydrocoupling reaction to produce soluble polymeric materials in 90% yield (Equation 6) [23]. The material is soluble in tetrahydrofuran or glyme and it can be precipitated subsequently by the addition of pentane to give a white powder ( $DP_n = 18$  to 43; 61% yield). This removes highly cross-linked structures in the initial polymer which are not soluble. Bulk pyrolyses of both the crude and recrystallized polymers heated under either argon or



ammonia to 1200°C have been found to result in the formation of white boron nitride powders in excellent purities and ceramic yields (85-93%; 95% theoretical ceramic yield). The materials produced at 1200°C exhibit diffuse reflectance IR spectra consistent with those previously reported for boron nitride, and densities (1.7-1.9 g/cm<sup>3</sup>) and x-ray powder diffraction patterns characteristic of turbostratic boron nitride.



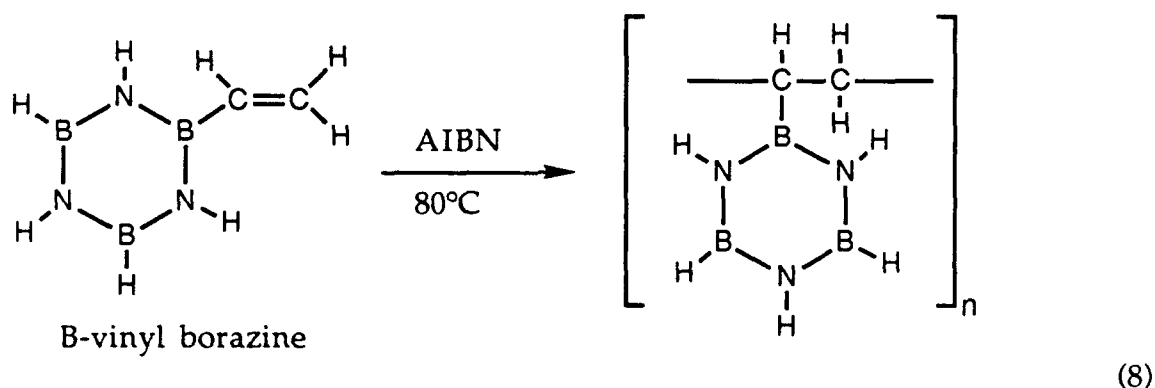
Another currently explored precursor is poly(borazinyll amine) from the condensation of trichloroborazine or N-alkyltrichloroborazine with hexamethyldisilazane (Equation 7) [9, 10, 12, 13, 19-21, 59]. Here the borazine rings are joined by either amino -N(H)- or alkylamino -N(R)- linkages. Routes containing aliphatic and aromatic diamine linkages have been reported but do not appear as promising due to the additional carbon which has to be removed [63-65]. Attempts to obtain reproducible molecular weight measurements on soluble fractions of poly(borazinyll amine) have been unsuccessful due to the relatively low solubility of the initial oligomers prior to solvent evaporation and complete insolubility in common organic solvents after vacuum drying [20]. TGA data suggest ceramic yields of 50-70% with heating to 1000°C. The off gases from pyrolysis of bulk samples are identified as solvent, ammonia, nitrogen, and hydrogen chloride [20, 58]. A lower ceramic yield is expected in comparison to polyborazylene in that poly(borazinyll amine) contains B:N ratio of 1:1.33. In addition, ring-opening reactions have been identified through <sup>15</sup>N isotope labeling of ring nitrogens [59].



Paciorek et al. [9], have reported that the conversion of B-trichloro-N-tris(trimethylsilyl) borazine to preceramic polymer failed to proceed rapidly and also

the polymer products obtained were infusible and insoluble. However, B-triamino-N-tris (trimethylsilyl) borazine yields preceramic polymers which are processable. Formation of boron nitride precursor fibers from these polymers by melt spinning techniques and conversion of the precursor fibers to boron nitride fibers by high temperature treatment in  $\text{NH}_3$  atmosphere have also been reported [8]. Paciorek et al., have obtained an infusible, but soluble, preceramic polymer by the reaction of trichloroborazine with hexamethyldisilazane in nonpolar solvents with rigid temperature control [10]. A high solubility of this polymer in solvents like pentane and hexane should offer the potential for a solution-based precursor fiber formation route. Infusibility could be a significant advantage in thermal conversion of the precursor fiber to the boron nitride fiber structure, as long as at low temperatures a stable solution can be maintained for solution spinning.

It has been found recently that soluble poly(vinyl borazine) can be obtained by solution polymerization of B-vinyl borazine with the free radical initiator, AIBN (Equation 8) [17, 54]. The synthesis of B-vinyl borazine has been recently made possible via the  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  catalyzed reaction of borazine with acetylene. The polymer is completely soluble in benzene or ether solvents. Molecular weight studies show  $M_w = 18,000$  and  $M_n = 10,700$  with some crosslinking or branching present. Pyrolysis of poly(vinyl borazine) under an ammonia atmosphere to  $1000^\circ\text{C}$  produces boron nitride with negligible carbon (ceramic yield 80%;  $\text{B}_{1.001}\text{N}_{1.01}\text{C}_{0.006}\text{H}_{0.04}$ ), whereas considerable carbon ( $\text{BNC}_{0.26}$ ) is retained if it is carried out under argon.



Another interesting method of producing precursor polymers for boron nitride as well as boron carbide ceramics has been developed by Seyferth et al. [14,15]. This method utilized the reactivity of decaborane ( $\text{B}_{10}\text{H}_{14}$ ) towards Lewis bases and involves condensation of diamines with decaborane to obtain processable polymeric materials. Solubility of these materials in common organic solvents and their melting points in the range of  $220\text{--}250^\circ\text{C}$  make them suitable candidates for producing ceramic precursor fibers. Depending on the environment in high

temperature consolidation, these precursors can yield boron nitride (in  $\text{NH}_3$ ) or boron carbide (in Argon).

### II.2.2. Polyborazylene

Polyborazylene is a poly(borazine) that is produced by dehydrogenation of borazine in vacuo at  $70^\circ\text{C}$ . Dehydrogenation is continued until the liquid becomes sufficiently viscous. It is then fully vacuum evaporated and recrystallized in pentane, leaving a white solid [23]. Polyborazylene is soluble in monoglyme or tetrahydrofuran.

1.2 grams of polyborazylene, precipitated from a solution with monoglyme, was received from Professor Sneddon of U. of Pennsylvania. Three analyses – thermogravimetric analysis (TGA) followed by x-ray diffraction, and infrared spectroscopy (KBr pellet) – were performed to infer appropriate conditions for thermochemical conversion after spinning. It was found that TGA in air to  $900^\circ\text{C}$  produced a ceramic material with a 95 wt% yield that showed an infrared spectrum (fig. 10) and an x-ray scattering pattern (fig. 11) similar to those found for turbostratic boron nitride [55]. As with polyborate, spinnable polyborazylene precursors to boron nitride may be formed with a low concentration of a high molecular weight polymer as a rheological aid which is fugitive during thermochemical conversion. An interesting feature of the untreated polyborazylene is that it has an x-ray diffraction pattern similar to turbostratic-BN even before thermochemical conversion.

Hand-drawn fibers were made from a 44.1 wt% polyborazylene and 51.0 wt% monoglyme solution with 4.9 wt% poly(ethylene oxide) (MW = 100,000). Preliminary experiments have shown that turbostratic boron nitride can be produced with a 95 wt% ceramic yield through thermochemical conversion of polyborazylene powder in air to  $900^\circ\text{C}$ .

### II.2.3. Polymer from Decaborane-Diamine

A polymer from decaborane and  $(\text{Me})_2\text{N}-\text{CH}_2-\text{CH}_2-\text{N}(\text{Me})_2$  was obtained from Dr. Seyferth of M.I.T. A morphological study of boron nitride fibers which had been formed through stress free consolidation of precursor fibers, obtained by hand drawing from solutions of precursor polymers, has been carried out. The diameter of the fibers was too large to be useful. Wide angle x-ray scattering, scanning electron microscopy and polarized optical microscopy show the structure of these brittle fibers to be amorphous and unoriented, with a highly porous morphology. The

analyses reveal clearly the need for effecting a uniaxial stress field during fiber formation and high temperature consolidation.

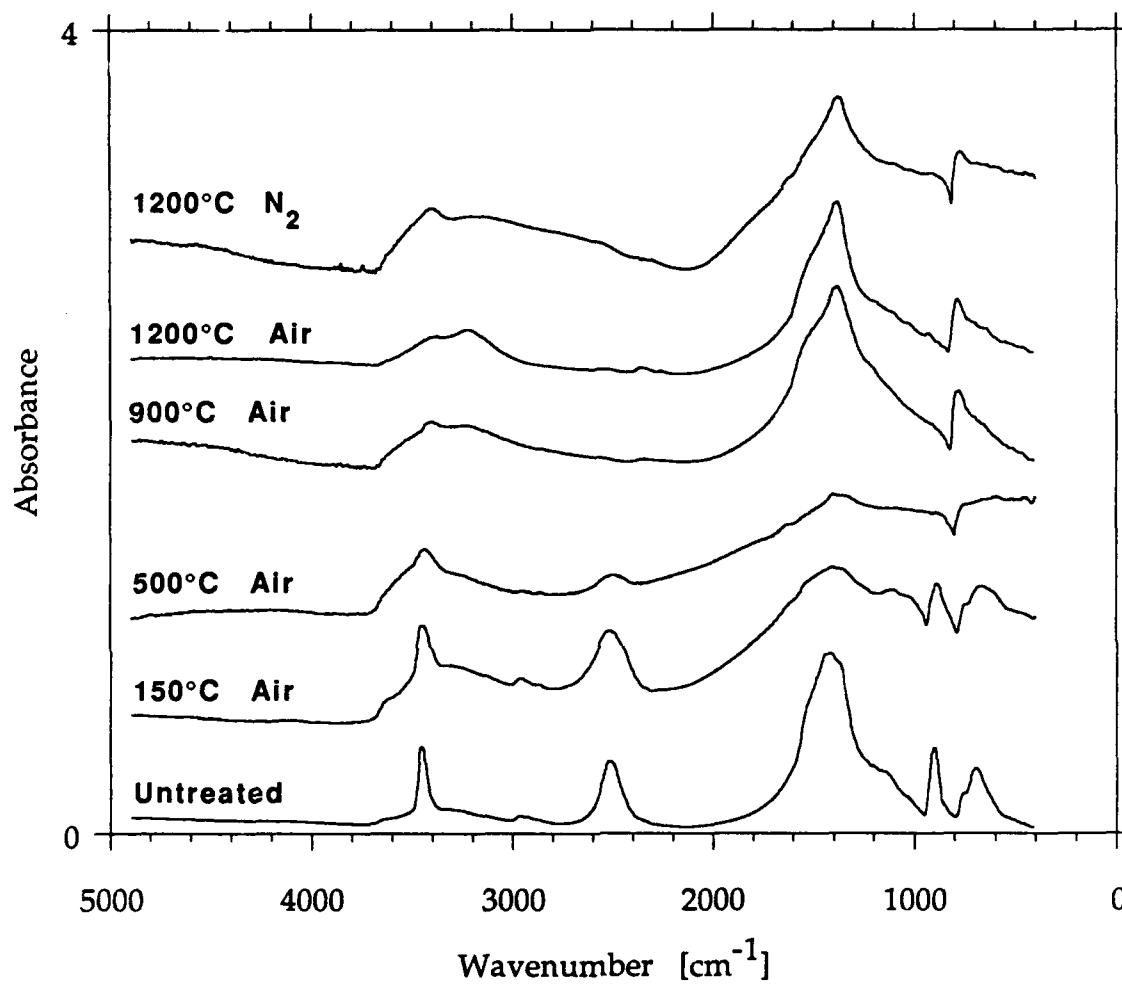


Fig. 10. FT-IR spectroscopy following the conversion of Polyborazylene to boron nitride at various temperatures.

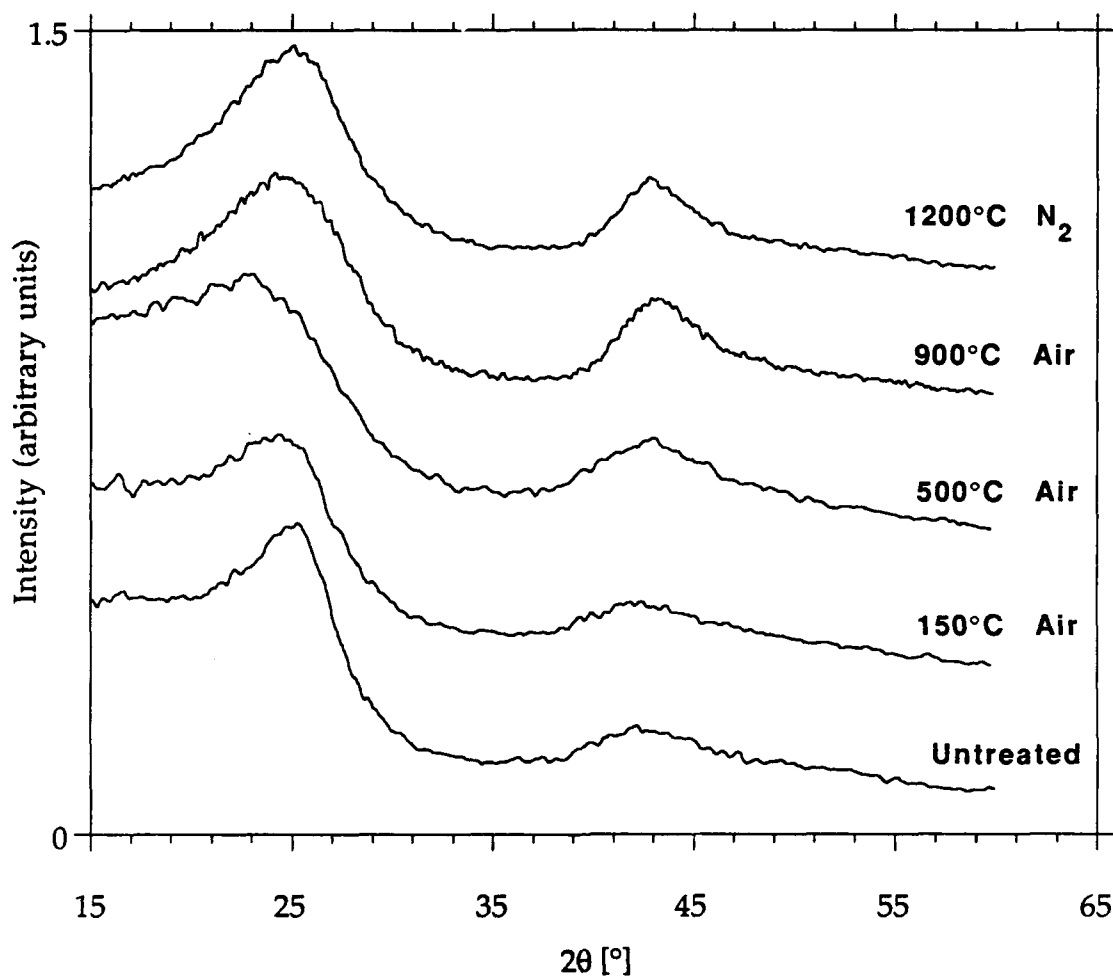


Fig. 11. Wide angle x-ray scattering following conversion of Polyborazylene to boron nitride at various temperatures.

### III. RESEARCH FACILITIES ESTABLISHED

Both bench-scale and small-scale equipments have been set up to conduct polymerization, solution formation, solution spinning of polyborate precursor fibers, and controlled thermo-chemical conversion of the precursor fibers to ceramic fibers at low, intermediate and high temperatures. This contributed to the development of an extensive research facility to examine formation of high performance fibers, not necessarily limited to boron nitride fiber formation. Facilities established for material production, fiber formation and thermal treatments, including consolidation, as a direct outcome of the present study, include polyborate synthesis reactor, exploratory scale melt and dry-solution fiber extrusion equipment, and a controlled heating rate test-scale tubular furnace for nitriding boron oxide fibers.

### IV. CONCLUSIONS AND RECOMMENDATIONS

In spite of the recent growth in research on the chemistry of precursor materials for ceramic structures, critical issues pertaining to continuous fiber formation and physical/chemical structures of the fibers remain largely unexplored. These are related to the chemistry of formation and spinnability of precursor materials, stability of precursor fluids, choice of precursor fiber formation routes, and effects of stress fields and environments during fiber formation and subsequent conversion to the desired ceramic structures. Fundamental studies of these aspects are necessary to build a base on which a broad range of fibrous structures can be developed most efficiently. Bringing together the appropriate expertise in materials synthesis, process engineering and material structures is essential in developing the required fundamental knowledge to effect a significant growth in the exciting field of ceramic fiber science and technology.

A fundamental difference exists between the formation of precursor fiber structures through the sol-gel transition and other conventional fiber formation processes which can be used with precursors for materials such as carbon and silicon carbide. The latter involves at the precursor spinning stage primarily physical transitions such as vitrification, crystallization or coagulation to effect the necessary fluid→solid transformation, whereas the sol-gel route requires appropriate combination of chemical reactions and physical transformation to cause the required change of state of the material in the extrusion process.

This study has examined various precursor polymer routes to boron nitride. Two candidate routes were selected for detailed studies on the basis of their compatibility with essential requirements for fiber formation.

- (i) Polyborate sol-gel fibers, as representing an oxide precursor to BN.
- (ii) Polyborazylene, a polymer of fused borazine polycyclic structures, as representing a non-oxide precursor to BN. Preliminary studies were also carried out with other materials, such as decaborane diamine precursors to BN.

The research here was guided exclusively by the need to produce continuous precursor fibers that can be processed ultimately to oriented boron nitride fibers. The following conclusions can be drawn in this regard.

#### A. Non-oxide routes

- Among the non-oxide precursors explored here, polyborazylene appears to be comparatively the most promising for the following reasons.

- (i) The precursor structure is close to the turbostratic structure desired in boron nitride. The transformation from the precursor polymer to BN appears to require chemical transformation without significant rearrangements within the basic morphological units.
- (ii) Spinnability of the precursor can be enhanced significantly by the addition of a rheological aid, such as poly(ethylene oxide), that would be fugitive during subsequent pyrolysis.

The polyborazylene precursor has, however, the following disadvantages.

- (i) It is relatively unstable and continues to polymerize even when it is refrigerated. Its hydrolytic stability is adequate for quick transfers in air.
- (ii) In spite of intuitive inferences that one might make regarding its high potential to be oriented in the precursor fiber form and thus transformed to the final BN fibers, preliminary experiments regarding fiber formation have not revealed any orientation.
- (iii) The high current cost of the precursor materials. The cost of borazine, commercially \$10 per gram, may limit the development of polyborazine precursor synthesis unless a cheaper route to this monomer is developed.
- (iv) It appears that solvents such as glyme and THF are very strongly bound with the polymer resulting in incomplete removal of the solvent. This results in residual carbon after conversion to ceramic.

- Precursors, such as decaborane-diamine, possess additional disadvantages (in comparison to polyborazylene) in that no natural mechanism can be inferred to exist for converting them to oriented BN fibers.

## B. Polyborate oxide routes

A polyborate network with a porous microstructure and without a counterion is expected to be a suitable precursor for high performance, boron nitride fibers. Since nitriding of boron oxide with ammonia is a diffusion controlled process [25], a porous boron oxide fiber structure from a sol-gel process may prove to be a suitable alternative to melt-extruded boron oxide fibers. The premise here is that the difficulty encountered by Economy in obtaining complete conversion of boron oxide to boron nitride, especially at the core of melt spun boron oxide fiber, would be eliminated by using a porous polyborate gel precursor fiber. However, whether the porous fiber structures can be deformed and consolidated during nitriding to produce dense, oriented boron nitride filaments remains to be explored.

The research reported here followed a logical progression from establishing the requirements for obtaining spinnable precursors with previously reported chemistry of polyborates with metal counterions, for example, lithium polyborates, through the development of methods to form spinnable polyborates without any metal counterions, to the formation and nitridation of continuous polyborate fibers. The following results are considered to be significant in this regard.

- Lithium polyborate gels have been synthesized from both tri-n-butyl borate and trimethoxyboroxine. A study of molecular structure using multinuclear NMR and IR indicates mechanistic similarities in the two sol-gel processes. Presence of tri-coordinate and tetracoordinate borons as well as the counterion environment can be conveniently examined by high resolution  $^{11}\text{B}$  NMR and  $^7\text{Li}$  NMR. Differential thermal analysis and x-ray diffraction studies indicate that a crystallized phase, approximating a mixed oxide phase of the composition of  $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ , was obtained from the lithium polyborate gels heat-treated to temperatures above  $600^\circ\text{C}$ .
- Fiber formation prior to gelation can be effected in polyborate sol-gel systems with lithium counterion. The fibers dry quickly in air and the gel fibers obtained are brittle. The potential for improved spinnability of such sols by the addition of high molecular weight polymer processing aids such as poly(N-vinyl pyrrolidinone) has been explored. Lithium polyborate fibers with porous microstructures have been obtained through sol-gel processes from tri-n-butyl borate as well as trimethoxyboroxine.
- Preliminary experiments revealed that controlled hydrolysis and polycondensation of trimethoxyboroxine led to the formation of viscous sols. The



partially hydrolysed polyborate structure obtained in the reaction seems to fulfil the requirements of providing better yields of boron oxide upon heat treatment, eliminating undesirable metal counterions, as well as showing better processibility in the context of fiber formation. Spinnability of these sols can be improved by the addition of poly(ethylene oxide) as a rheological aid. IR and TGA results indicated that sol-gel derived precursors to a single-component boron oxide system can be obtained by the partial hydrolysis and polycondensation involving trimethoxyboroxine.

- The formation of a meltable polyborate precursor was achieved by the direct polycondensation of trimethoxyboroxine and boric acid with the addition of about 2 wt % high molecular weight poly(N-vinylpyrrolidinone) (PVP, MW = 360,000). Reactions with a 1:1 stoichiometry of trimethoxyboroxine to boric acid on cooling result in precipitation of boric acid. This is because of trimethyl borate-methanol azeotrope formation (~1:1 mole ratio) and concurrent hydrolysis of trimethoxyboroxine with polycondensation. Stoichiometries of 2:1 to 3:1 have been successfully employed for spinning at 135°C. Polyborate fibers melt spun from the thermoplastic polyborate composition are much more resistant to further hydrolysis to boric acid in room air than those drawn from solutions of either tetrahydrofuran or monoglyme. When heated above 54.6°C, the boiling point of the azeotrope, continued condensation in the polyborate fibers results in thermochemical conversion to boron oxide fibers. Batch nitrided samples of polyborate fibers show evidence of a partially nitrided structure after 200°C. X-ray diffraction of polyborate fibers after nitriding to 700°C shows a turbostratic-like boron nitride pattern.

- An appropriate synthesis route that did not require an organic solvent was sought in order to eliminate a source of carbonaceous residues. It was found that PVP was not soluble when trimethoxyboroxine was disproportionated in the absence of added boric acid, thus not producing methanol. Methanol alone is a good solvent for PVP. It appears that PVP requires methanol for compatibility with polyborate. Therefore, other candidate polymers to use as rheological aids were examined, including poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc). They were found to be completely soluble with trimethoxyboroxine and, therefore, either polymer can be directly used in the disproportionation synthesis to obtain a spinnable polyborate. PVAc, however, is not expected to be completely fugitive during thermochemical conversion. It leaves a 25 wt. % carbonaceous residue on heating to 400°C in air. PMMA is completely lost under the same conditions.

- The polyborate route currently offers a more economical route to make boron nitride fibers in comparison to polyborazylene. Spinnable polyborate formulations have been obtained through polycondensation of trimethoxyboroxine and boric acid. Trimethoxyboroxine is available commercially for 12¢ per gram. Boric acid is available commercially for less than 10¢ per gram depending on the purity desired.

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**APPENDIX I.**  
**PAPERS AND PRESENTATIONS RESULTING FROM:**  
**"FORMATION, STRUCTURE AND PROPERTIES OF**  
**BORON NITRIDE FIBERS FROM POLYMER PRECURSORS"**

**PUBLICATIONS AND PRESENTATIONS**

**REFEREED PUBLICATIONS**

1. "Synthesis and Characterization of Spinnable Sol-Gel Derived Polyborates," N. Venkatasubramanian, Bruce Wade, P. Desai, A. S. Abhiraman and L. T. Gelbaum, *Journal of Non-Crystalline Solids*, **130**, 144-156 (1991).
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1. "Synthesis and characterization of spinnable sol-gel derived polyborates," N. Venkatasubramanian, Bruce Wade, P. Desai, A. S. Abhiraman, and L. T. Gelbaum, *Polym. Mater. Sci. Eng.*, **62**, 614-19 (1990).
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3. "Boron Nitride Fibers from Polyborates", Bruce Wade, D. Mohr, N. Venkatasubramanian, P. Desai, and A. S. Abhiraman, *Polymer Preprints*, **32(3)**, 554-555 (1991).

**PRESENTATIONS**

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**APPENDIX II.**  
**REPRINTS OF PAPERS RESULTING FROM:**  
**"FORMATION, STRUCTURE AND PROPERTIES OF**  
**BORON NITRIDE FIBERS FROM POLYMER PRECURSORS"**

## Synthesis and characterization of spinnable sol-gel derived polyborates

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Polyborate sol-gel routes have been studied in the context of molecular structure development and spinnability of the sols obtained through the sol-gel process. The similar chemical structures of the lithium polyborates derived from lithium methoxide and tri-*n*-butyl borate or from lithium methoxide and trimethoxyboroxine suggest mechanistic similarities in the two sol-gel reactions. Identical mixed oxide compositions could be formed by heat treatment of the lithium polyborate gels obtained in the two reactions. A controlled hydrolysis and polycondensation of trimethoxyboroxine has also been investigated to form polyborates without the presence of a counterion. The porous gel filaments that can be drawn from these sols may be suitable as precursors for the formation of other ceramic structures such as boron nitride.

### 1. Introduction

In recent years, considerable progress has been made in the synthesis of glasses and ceramics through the sol-gel route involving the hydrolysis and polycondensation of metal alkoxide solutions. The advantages associated with this process [1], to state just a few, include: (a) lower temperature fabrication of materials relative to melt processing of oxide compositions; (b) formation of mixed oxide compositions not obtainable by melt processing; (c) suitability for making ultrapure glasses and ceramics; (d) homogeneity attainable by mixing of monomers in the liquid state; and (e) the capability to form a variety of shaped end-products such as thin films, fibers, monoliths, spheres and powders.

Gel fibers obtained through the sol-gel process

from viscous metal alkoxide solutions serve as precursors for oxide fibers [2]. It is important to identify the composition of metal alkoxide solutions that become spinnable in the course of hydrolysis and condensation [3]. Fibers of the systems  $\text{SiO}_2$ ,  $\text{SiO}_2\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2\text{-ZrO}_2$  and  $\text{ZrO}_2$  and others have been prepared by this route [4-6]. High molecular weight organic polymers, such as poly(vinyl alcohol) and poly(ethylene oxide), have been used to control rheology and increase the spinnability of sol-gel derived precursors to ceramic oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3\text{-SiO}_2$  [7] and  $\text{ZrO}_2$  [5].

The current investigation involves studies related to molecular structure development as well as fiber formation in polyborate sol-gel systems. The former aspect involves understanding structure development on a molecular scale by suitable spectroscopic and allied techniques. Multicomponent oxide ceramic fibers incorporating borates are used in reinforcement of polymers, ceramics

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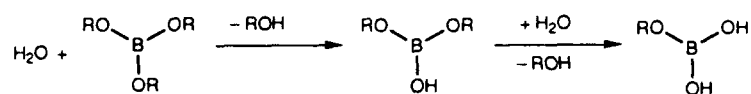


and metals [8]. Known applications of borate-containing glasses include coatings in the electronics industry [9] and as flame-retardant additives. Formation of fibers from polyborate sols and chemical conversion of sol-gel derived boron oxide fibers to boron nitride fibers [10] are envisaged as a possible application.

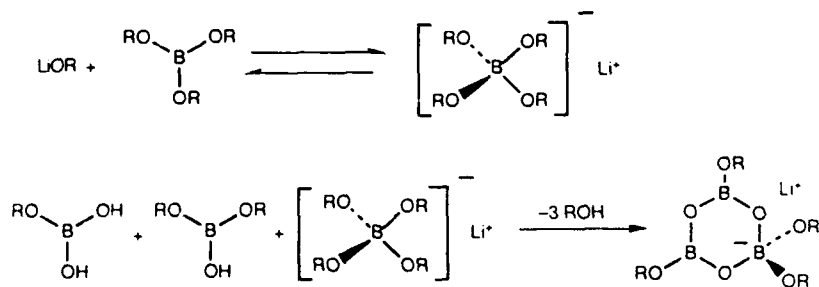
Unlike silicon alkoxides, boron alkoxides hydrolyze rapidly resulting in precipitation of boric acid, making the usual hydrolysis and polycondensation route ineffective for the formation of polyborate gels [11]. Studies by Weinberg et al. [11] and Brinker et al. [12,13] have demonstrated the formation of borate gels by the reaction of trialkyl borates with lithium methoxide in a mixed

alcohol and water solvent system. The postulates by Edwards and Ross [14] define the restrictive structural requirements for the formation and stability of hydrated polyborates. The ability to form a trimeric ring containing both tricoordinate and tetracoordinate borons and the stability of the tetracoordinate borons in a hydrolytic environment are important criteria for the formation of polyborate structures. An illustration of one of the mechanistic possibilities for the lithium polyborate sol-gel process involving a trialkyl borate is provided by Brinker in a simplified scheme (fig. 1, [12]). Condensation presumably occurs by the nucleophilic attack of the alkoxy oxygen attached to tetracoordinate boron on the electrophilic trico-

(i) Partial hydrolysis of borate precursor:



(ii) Condensation to form primary units:



(iii) Linkage of units to form polymer network:

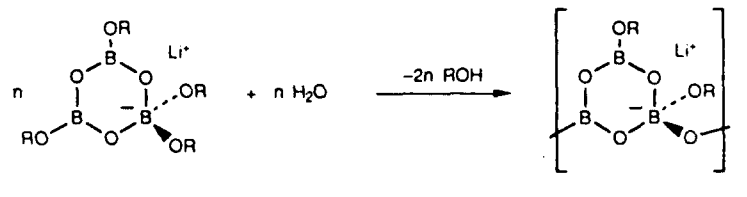


Fig. 1. Lithium polyborate sol-gel reaction from trialkyl borate (mechanism adapted from ref. [12]).

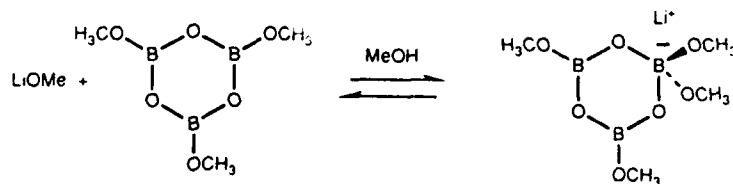
ordinate boron carrying the hydroxyls formed by hydrolysis [12].

In the present study, the lithium polyborate sol-gel process has been investigated in detail using tri-*n*-butyl borate as well as trimethoxyboroxine (a six-membered cyclic boron alkoxide) as starting materials. The advantage of the metaborate is that it can directly form the primary structural unit with lithium alkoxide by complexation using ambient humidity to induce the hydrolysis and polycondensation reaction sequence (fig. 2), whereas tri-*n*-butyl borate would require controlled initial addition of water to the reaction mixture for partial hydrolysis leading to the formation of the cyclic trimer in a subsequent condensation step (fig. 1). The initial proportions of the reactants were chosen so as to obtain a gel-forming binary oxide composition [11,12] that can be used as a model system to examine the concepts involved in polyborate formation. The transformations occurring during the consolidation of the lithium polyborate gels obtained from tri-*n*-butyl borate as well as trimethoxyboroxine have been studied using thermal analyses and X-ray diffrac-

tion. The sol-gel reaction of trimethoxyboroxine incorporating sodium as counterion has also been examined to infer the general applicability of this process.

Toward the objective of producing boron oxide fibers that can serve as precursors for the formation of boron nitride fibers, the possibilities for the formation of a sol-gel derived polyborate without the presence of a counterion in the polyborate structure have also been investigated. Synthetic methods for the formation of sol-gel derived boria (without the counterion in the polyborate structure) in analogy to silica, alumina, titania, etc., were explored by a partial hydrolysis and polycondensation route involving trimethoxyboroxine. Alternatively, this objective can be accomplished by synthesizing polyborates with an ammonium counterion instead of an alkali metal counterion in the polyborate structure, since the former can be eliminated as ammonia, providing a metal-free boron oxide precursor for nitriding. Preliminary experiments to incorporate ammonium counterion by a sol-gel route involving trimethoxyboroxine and ammonium hydroxide as

(i) Complexation with LiOMe:



(ii) Hydrolysis-Polycondensation to form a polymer network:

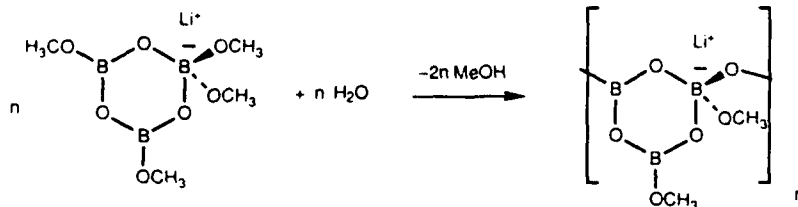


Fig. 2. A probable scheme for lithium polyborate sol-gel reaction from trimethoxyboroxine.

well as by a metal-ammonium counterion exchange have been carried out.

## 2. Experimental

### 2.1. Materials

Tri-*n*-butyl borate, absolute methanol (low-acetone grade) and lithium methoxide were obtained from Alfa Products. Sodium methoxide was obtained from Aldrich Chemical Company. Trimethoxyboroxine samples used for sol-gel investigations were obtained from Aldrich and Callery Chemical Companies. Poly(ethylene oxide) with a weight average molecular weight of 100 000 and poly(*N*-vinylpyrrolidinone) with a weight average molecular weight of 360 000 were obtained from Aldrich. They were found to be suitable for use in sol-gel reactions as polymeric processing additives in tetrahydrofuran (THF) and methanol, respectively.

### 2.2. Lithium polyborate from tri-*n*-butyl borate

The procedure employed was similar to the one reported by Weinberg et al. [11] for the formation of a binary oxide with the molar composition of  $0.30\text{Li}_2\text{O} \cdot 0.70\text{B}_2\text{O}_3$ . Lithium methoxide (0.066 mol) was dissolved in methanol (0.616 mol) and freshly distilled water (0.140 mol). Tri-*n*-butyl borate (0.154 mol) was added dropwise to the above solution. After mixing at room temperature, the clear sol was aged at 50°C in a 95% relative humidity environment. Fibers could be drawn from the viscous, translucent sol after 12 h (Sol 1). The drawn fibers were air dried at room temperature to produce dried fibers. A part of the sol was dried at 90°C in vacuum for 12 h to obtain a white powder. When a sol of the same initial composition was aged at room temperature in 100% relative humidity (Sol 2), gelation occurred in 18 h.

### 2.3. Lithium polyborate from trimethoxyboroxine

A nearly 1:1 molar ratio of trimethoxyboroxine and lithium methoxide was used for the reaction. Trimethoxyboroxine (0.090 mol) was added

dropwise to lithium methoxide (0.085 mol) in methanol (0.790 mol) and the mixture was aged in 100% relative humidity at room temperature (Sol 3). Fibers could be drawn from the transparent sol prior to gel formation that occurred in 20 h. The drawn fibers were air dried at room temperature to obtain dried fibers. A part of the sol was also dried in vacuum at 90°C to obtain dried powder.

### 2.4. Lithium polyborate from trimethoxyboroxine in presence of a rheological aid

0.24 g of poly(*N*-vinylpyrrolidinone), 2 wt% relative to the weight of trimethoxyboroxine (11.95 g, 0.068 mol) was dissolved in a solution of lithium methoxide (0.068 mol) in excess methanol (0.740 mol). Trimethoxyboroxine was added dropwise to the above solution which was aged at 100% relative humidity at room temperature. A viscous sol was obtained after 30 h aging. Long fibers could be drawn from the sol using a glass rod.

### 2.5. Sodium polyborate from trimethoxyboroxine

Polyborate incorporating sodium ion was synthesized by aging a reaction mixture of trimethoxyboroxine (0.055 mol) and sodium methoxide (0.053 mol) in methanol (0.469 mol) at room temperature in a 100% relative humidity atmosphere. Gelation occurred in 20 h. The sol was dried as described earlier.

### 2.6. Partial hydrolysis and polycondensation of trimethoxyboroxine

The formation of polyborate in the absence of a counterion was investigated by addition of water (0.086 mol) in 100 ml THF to trimethoxyboroxine (0.172 mol). A viscous sol was found to result after solvent removal at 60°C in partial vacuum. However, the sol exhibited poor spinnability, apparently due to insufficient molecular weight. The same experiment was carried out with the inclusion of 0.5 g (1.6 wt% relative to trimethoxyboroxine) of high molecular weight poly(ethylene oxide) as a polymer additive in the initial reaction mixture. Long fibers could be hand-drawn from the viscous sol with a glass rod.

### 2.7. Attempted ammonium polyborate sol-gel reaction

10 ml aqueous ammonium hydroxide (0.148 mol) was mixed in excess THF (0.90 mol) and the mixture was added dropwise to trimethoxyboroxine (0.148 mol). This resulted in instantaneous formation of a precipitate which was filtered and dried.

### 2.8. Characterization

$^{11}\text{B}$  NMR spectra of the reaction mixtures (sols) were obtained using a Varian XL-400 NMR spectrometer operating at 128.311 MHz. When possible, quartz NMR tubes were used to minimize the broad borosilicate glass background. The boron resonances were externally referenced to proton-decoupled  $^{11}\text{B}$  NMR spectrum of 0.25M sodium borohydride in tetraglyme ( $-41.0$  ppm with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  defined as 0.0 ppm). The delay time of 10 s used in the  $90^\circ$  pulse experiment was at least five times longer than the average spin-lattice relaxation time,  $T_1$ , of the boron nuclei to ensure that the data would be quantitative.  $^7\text{Li}$  NMR spectra were obtained at an operating frequency of 155.454 MHz using, as an external reference, a mixture of a 2 ml solution of 0.85M LiBr in tetraglyme and 1 ml acetone- $d_6$  (0.59 ppm relative to 0.5M LiCl in  $\text{D}_2\text{O}$  defined as 0.0 ppm) or a mixture of a 1 ml solution of 0.85M LiBr in tetraglyme and 2 ml acetone- $d_6$  (0.70 ppm relative to 0.5M LiCl in  $\text{D}_2\text{O}$  defined as 0.0 ppm). A pulse delay of 10 s was applied in a  $45^\circ$  pulse experiment. The viscous polyborate Sol 1 was dissolved in 1-methyl-2-pyrrolidinone (NMP) and the  $^{11}\text{B}$  and  $^7\text{Li}$  NMR spectra of this solution were also obtained. Unless otherwise stated, all NMR spectra were obtained at ambient temperature. IR spectra (KBr pellet) of the polyborate fiber as well as those of the dried polyborate gel powder and the heat treated gel samples were obtained using a Nicolet 60SX FT-IR system.

In addition to the spectroscopic methods described above, thermal analyses (TGA and DTA using Perkin-Elmer thermal analyzers), scanning electron microscopy (Cambridge Stereoscan 90) and wide angle X-ray diffraction (Rigaku D/

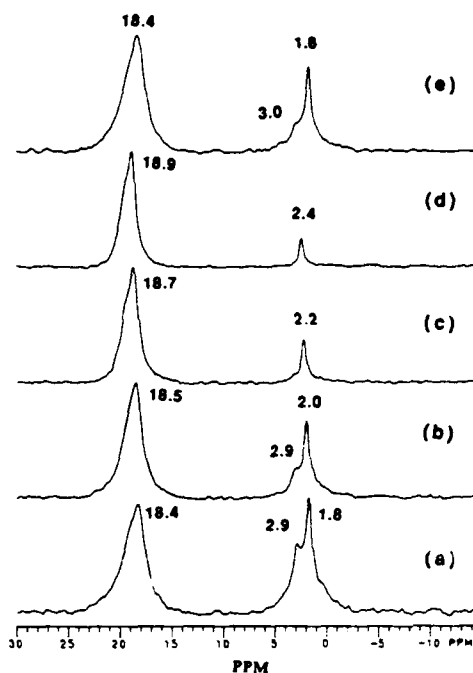


Fig. 3.  $^{11}\text{B}$  NMR spectra of a 50 vol.% lithium polyborate sol (Sol 1) in NMP at different temperatures: (a)  $20^\circ\text{C}$ , (b)  $40^\circ\text{C}$ , (c)  $60^\circ\text{C}$ , (d)  $80^\circ\text{C}$ , and (e) cooled back to  $20^\circ\text{C}$ . An external reference of 0.25 M  $\text{NaBH}_4$  in tetraglyme at  $-41.0$  ppm (relative to  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  defined as 0.0 ppm) was used.

Max-B system operating at 45 kV and 100 mA using Ni-filtered  $\text{Cu K}\alpha$  radiation) were used for the characterization of the sol-gel derived borates.

## 3. Results and discussion

### 3.1. NMR analyses of sol-gel process with tri-*n*-butyl borate

$^{11}\text{B}$  NMR studies are useful for identifying tricoordinate and tetracoordinate boron environments [15] in the polyborate structures generated by the sol-gel process. A 50 vol.% solution of the viscous, fiber-forming Sol 1 in NMP (fig. 3) shows the presence of tricoordinate borons at a resonance of 18.5 ppm and a high field resonance at 1.8 ppm due to tetracoordinate borons in the borate structure. The resonance at 2.9 ppm presumably arises due to the coordination of the amide solvent with the tricoordinate borons in the

polyborate structure creating an additional tetra-coordinate boron environment in the sol. The relative intensities of the borate resonances seem temperature-dependent with the complete disappearance of the 2.9 ppm resonance with an increase in temperature to 80°C and its reappearance when the NMR sample is cooled back to 20°C (fig. 3). An independent  $^{11}\text{B}$  NMR study (figs. 4(a) and (b)) of the lithium polyborate Sol 2, obtained by aging for 6 h at room temperature, demonstrates that the fraction of the tetra-coordinate borons in the borate sol is increased (as inferred from the appearance of the new boron resonance at 2.9 ppm) when NMP is added to the sol. This was also confirmed by additional  $^{11}\text{B}$  NMR experiments with 50 vol.% solutions of trimethoxyboroxine in NMP and dimethylformamide (DMF) which revealed the presence of tetra-coordinate boron resonances, although much lower in intensity, at 2.3 ppm and 3.7 ppm, respectively, besides the major resonance at 18.5 ppm for the tricoordinate borons in trimethoxyboroxine.

An estimate of the ratios of the tricoordinate and tetra-coordinate borons can be obtained from the integrated intensities of the resonances in the  $^{11}\text{B}$  NMR spectra. If the polyanionic borate con-

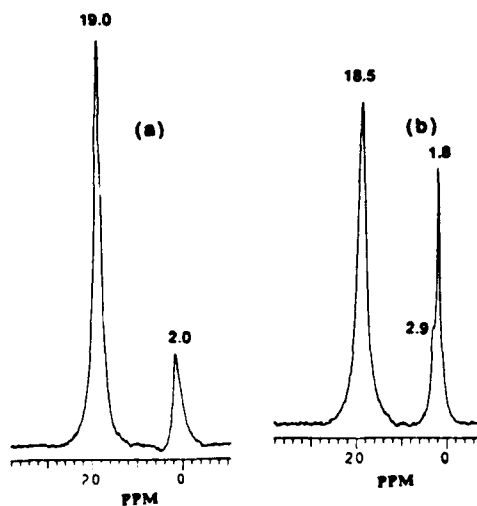


Fig. 4.  $^{11}\text{B}$  NMR spectra of (a) lithium polyborate sol (Sol 2) aged for 6 h at room temperature and (b) 66 vol.% of the same sol in NMP.

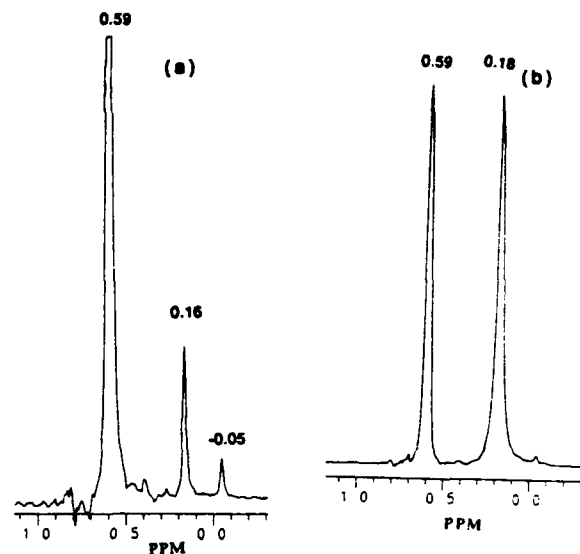


Fig. 5.  $^7\text{Li}$  NMR spectra of (a) 50 vol.% lithium polyborate sol (Sol 1) in NMP and (b) a mixture of  $\text{LiOMe}/\text{MeOH}/\text{H}_2\text{O}$  (1:9:2 molar ratio). An external reference of a mixture of 2 ml 0.85 M  $\text{LiBr}$  in tetraglyme and 1 ml acetone- $d_6$  was used (0.59 ppm relative to 0.5 M  $\text{LiCl}$  in  $\text{D}_2\text{O}$  defined as 0.0 ppm).

sisted only of the cyclic trimer structure in the backbone as indicated in fig. 1, the fraction of the tetra-coordinate borons in the polyborate would be close to 0.33. The fraction of tetra-coordinate borons calculated from NMR was found to be 0.18 in the case of lithium polyborate Sol 2, aged 6 h at room temperature (fig. 4(a)). This indicates that there are borate structural units other than the cyclic trimer also present in the sol-gel derived polyborates. The  $^{11}\text{B}$  NMR studies can differentiate between tricoordinate and tetra-coordinate borons but show no direct evidence for cyclic or linear structures in the polyborate. However, the presence of boroxine ring structure has been identified for polyborate ions in solution by Raman spectroscopy [16], and comparisons have also been made in the literature with the known structures for hydrated borates from X-ray diffraction [16].

The counterion environment in Sol 1 (50 vol.% in NMP) was examined by  $^7\text{Li}$  NMR using as external reference the  $^7\text{Li}$  resonance at 0.59 ppm due to  $\text{LiBr}$ . Figure 5(a) shows two main resonances at -0.05 ppm and 0.16 ppm which were

assigned, respectively, to the lithium counterion in the tetracoordinate borate environment and lithium ion in LiOH due to hydrolysis of LiOMe. Figure 5(b) shows the  $^7\text{Li}$  NMR spectrum of a hydrolyzed mixture of LiOMe in MeOH, the relative proportions of LiOMe, MeOH and  $\text{H}_2\text{O}$  being the same as used for the reaction. Apparently, in the process of the formation of the polyborate sol from trialkyl borates (fig. 1), a fraction of LiOH remains unreacted in the equilibrium leading to the formation of the tetracoordinate borate complex [12] since tri-*n*-butyl borate is added to a pre-hydrolyzed mixture of LiOMe and MeOH to form the initial sol.

### 3.2. NMR analyses of sol-gel process with trimethoxyboroxine

As indicated in fig. 2, complexation of trimethoxyboroxine with LiOMe followed by hydrolysis and polycondensation in a humid atmosphere provides a plausible route for the formation of a polyborate structure. In the  $^{11}\text{B}$  NMR spectrum of Sol 3 (aged for 3 h, no added solvent), the tetracoordinate boron appears at 1.8 ppm and the tricoordinate boron appears as a broad resonance centered at 12.8 ppm (figure 6(a)). In the corresponding  $^7\text{Li}$  NMR spectrum (fig. 6(b)), the dominant resonance (besides that of the external reference at 0.70 ppm due to LiBr) is that of the lithium counterion in the tetracoordinate borate environment at -0.13 ppm. The  $^{11}\text{B}$  NMR of the sol before aging (initial sol) shows the presence of tetracoordinate borons at 1.9 ppm and the tricoordinate borons at 13.6 ppm (fig. 7(a)). The counterion in the tetracoordinate borate anion complex appears as the major resonance at -0.10 ppm in the  $^7\text{Li}$  spectrum (fig. 7(b)). There was no LiOH resonance observed in these sols. Since no water was initially added in the sol-gel reaction, LiOMe and trimethoxyboroxine appear to have reacted in a 1:1 molar ratio, in the formation of the initial complex (fig. 2). However, the simplified scheme for lithium polyborate formation from trimethoxyboroxine (fig. 2) does not take into consideration reactions such as methanolysis of trimethoxyboroxine [17] which would explain the formation of some boric acid (confirmed by IR)

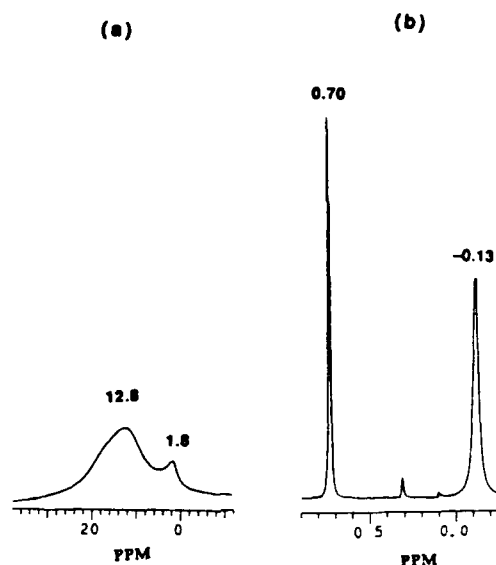


Fig. 6. (a)  $^{11}\text{B}$  NMR spectrum of lithium polyborate sol (Sol 3) aged for 3 h at room temperature and (b)  $^7\text{Li}$  spectrum of the same sol; an external reference of a mixture of 1 ml 0.85 M LiBr in tetraglyme and 2 ml acetone- $\text{d}_6$  was used (0.70 ppm relative to 0.5 M LiCl in  $\text{D}_2\text{O}$  defined as 0.0 ppm).

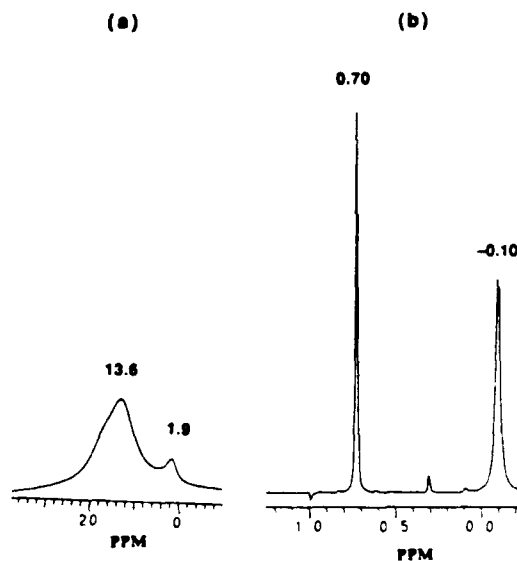


Fig. 7. (a)  $^{11}\text{B}$  NMR spectrum of lithium polyborate sol (Sol 3) before aging and (b) the corresponding  $^7\text{Li}$  NMR (external reference same as in fig. 6).

that was deposited on the walls of the container during the aging process. The boron loss observed during the reaction precludes reliable theoretical estimates of final compositions based on the proportions of trimethoxyboroxine and LiOMe in the initial reaction mixture.

### 3.3. Structural information from FTIR

The IR (KBr pellet) spectra of the air dried borate fiber drawn from Sol 1 and the dried gel from trimethoxyboroxine (Sol 3) show identical features (figs. 8(a) and (b)). The tricoordinate B-O stretch occurs at  $1354\text{ cm}^{-1}$  and the other dominant bands are attributed to the tetracoordinate borate stretch at  $1028\text{ cm}^{-1}$  and the O-H stretch at  $3434\text{ cm}^{-1}$  [11]. The weaker bands in the spectra occur around  $1630\text{ cm}^{-1}$  (assigned to the deformation mode for the hydroxyl group [11]) and as a shoulder at  $895\text{ cm}^{-1}$ . Dried sodium polyborate gel (not shown) has an IR spectrum indistinguishable from those of the lithium polyborates. In these spectra, no C-H absorption due to the alkoxy groups is observed, indicating that the dried gels may have fully hydrolyzed and partially condensed polyborate structures.

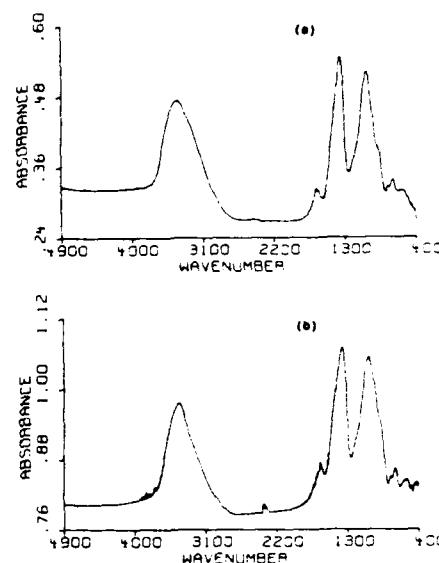


Fig. 8. IR spectra of (a) dried lithium polyborate fiber from Sol 1 and (b) dried gel from Sol 3.

### 3.4. Heat treatment of sol-gel derived lithium polyborates

The thermogravimetric analyses in air of the lithium polyborate gels from Sol 1 and Sol 3 at a

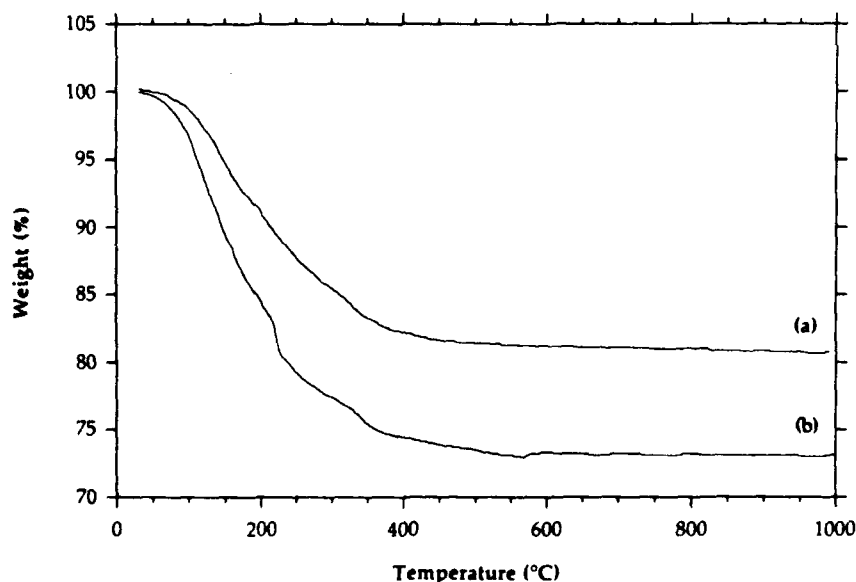


Fig. 9. TGA in air at a heating rate of  $10^{\circ}\text{C}/\text{min}$  of (a) lithium polyborate gel from Sol 1 and (b) the corresponding gel from Sol 3.

heating rate of  $10^{\circ}\text{C min}^{-1}$  show weight losses of 19% and 27%, respectively. These changes seem to occur completely below a temperature of  $550^{\circ}\text{C}$  (fig. 9). Based on the initial molar proportions of tri-n-butyl borate and lithium methoxide used in the reaction, the calculated weight loss for the formation of the expected mixed oxide composition of  $0.30 \text{ Li}_2\text{O} \cdot 0.70 \text{ B}_2\text{O}_3$  by a simple stoichiometric decomposition of a mixture of lithium hydroxide and boric acid would be 43%. Since the observed weight loss in the TGA is much lower (19%) for the lithium polyborate during heat treatment, the dehydration presumably occurs from the structural units of a polyborate network rather

than from monomeric species. Differential thermal analyses of the two borates in air at a heating rate of  $10^{\circ}\text{C min}^{-1}$  (figs. 10a and (b)) reveal crystallization exotherms at  $540^{\circ}\text{C}$  and the onset of melting in the  $800\text{--}830^{\circ}\text{C}$  range. The X-ray diffraction scan of the lithium polyborate gel (derived from trimethoxyboroxine) heat treated up to  $625^{\circ}\text{C}$  (fig. 11(a)) reveals the formation of a crystallized phase approximating the structure observed for a phase with the composition of  $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$  [11,18]. The sample heated to  $500^{\circ}\text{C}$  has considerably less crystallinity as shown by XRD (fig. 11(b)). An identical crystallization behavior (not shown) was exhibited by the lithium poly-

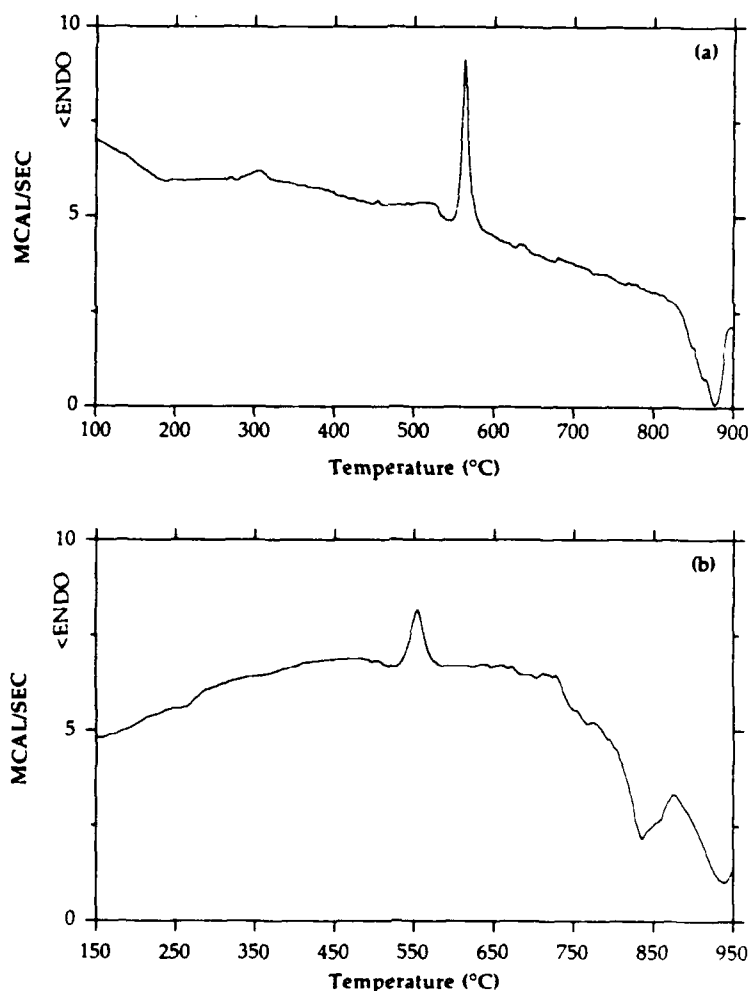


Fig. 10. DTA in air at a heating rate of  $10^{\circ}\text{C/min}$  of (a) lithium polyborate gel from Sol 1 and (b) the corresponding gel from Sol 3.



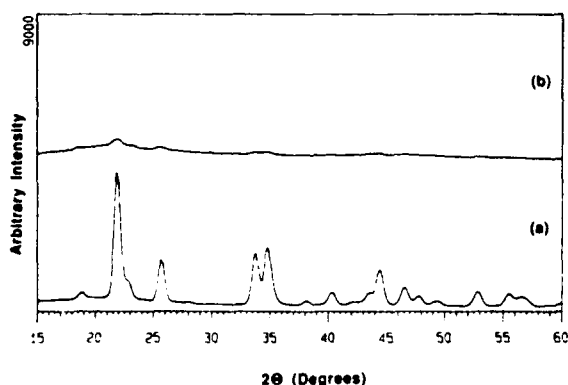


Fig. 11. XRD scans of (a) lithium polyborate gel (derived from Sol 3) heated to 625°C and (b) lithium polyborate gel (derived from Sol 3) heated to 500°C.

borate gel (derived from tri-*n*-butyl borate, Sol 1) heated to 625°C. An inspection of the IR spectrum (KBr pellet) of the lithium borate sample (derived from trimethoxyboroxine, Sol 3) heat treated to 625°C (fig. 12(a)) shows a shift in the tricoordinate borate stretch to 1385  $\text{cm}^{-1}$  relative to the untreated, dried gel (fig. 8(b)). The dominant tetracoordinate borate stretch occurs at 980  $\text{cm}^{-1}$  and two other separate maxima of lower

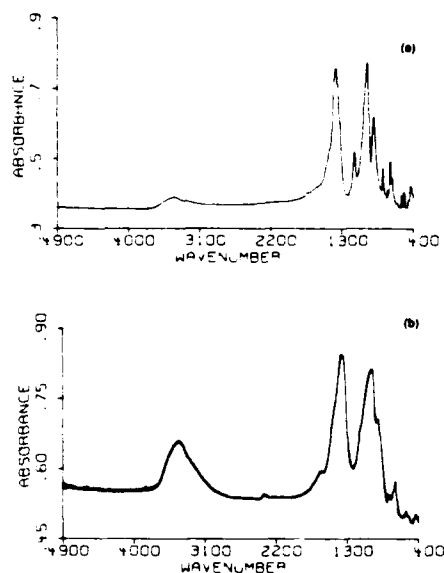


Fig. 12. IR spectra of (a) lithium polyborate gel (derived from Sol 3) heated to 625°C (b) the gel from Sol 3 heated to 500°C.

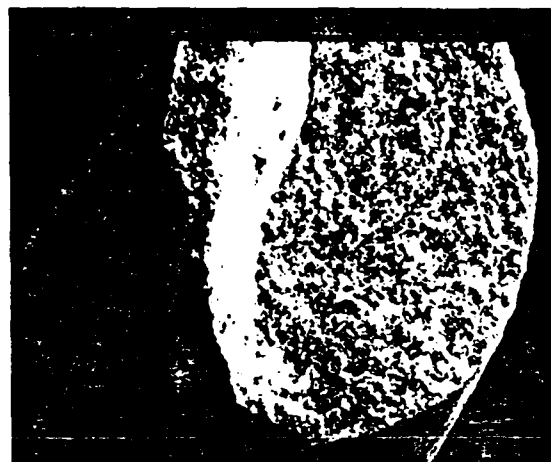


Fig. 13. SEM of the cross-section of lithium polyborate fiber from Sol 1.

intensities are found to occur at 1140  $\text{cm}^{-1}$  and 905  $\text{cm}^{-1}$ . This spectrum resembles the IR spectrum of anhydrous crystalline  $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$  reported in the literature [19]. The IR spectrum of the sample heat treated up to 500°C (fig. 12(b)) has a distinct hydroxyl absorption of 3437  $\text{cm}^{-1}$  and the various absorptions due to the borate structure occur at 1370  $\text{cm}^{-1}$ , 992  $\text{cm}^{-1}$  and 907  $\text{cm}^{-1}$ .

### 3.5. Microstructure of the fibers

Microstructural examination of the sol-gel derived fiber samples by scanning electron microscopy shows that both the cross-section and the surface of the fiber from Sol 1 are highly porous (figs. 13 and 14). A similar porous structure is also found in the cross-section of the fiber drawn from Sol 3 (fig. 15) although the surface appears to be more dense.

### 3.6. Hydrolysis and polycondensation of trimethoxyboroxine

Exploratory experiments in the partial hydrolysis and polycondensation of trimethoxyboroxine resulted in the formation of a viscous polyborate sol without the requirement of a counterion. The spinnability of the sol was greatly enhanced by

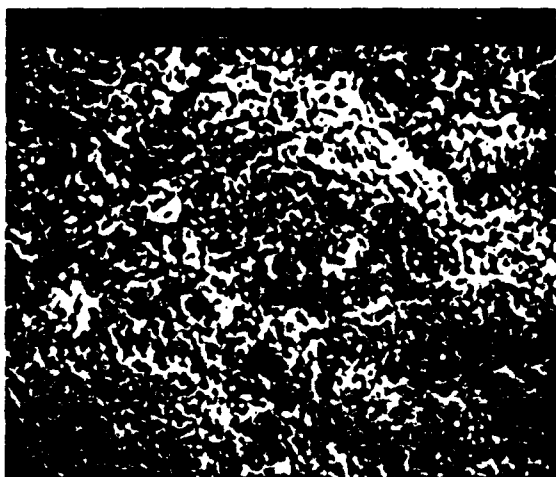


Fig. 14. SEM of the surface of lithium polyborate fiber from Sol 1.

incorporating poly(ethylene oxide) as a polymer processing aid. The IR spectrum of the viscous sol taken using AgCl plates (fig. 16(a)) shows a reduction in C-O stretch at  $1080\text{ cm}^{-1}$  relative to the reactant trimethoxyboroxine (fig. 16(b)) indicating partial hydrolysis. The IR also distinctly indicates the presence of the hydroxyl group at  $3421\text{ cm}^{-1}$  as well as that of the unreacted methoxy C-H bands at  $2970\text{ cm}^{-1}$ ,  $2881\text{ cm}^{-1}$  and  $1486\text{ cm}^{-1}$ . The B-O stretch of the boroxine ring is observed in the sol (fig. 16(a)) in the region  $1300\text{--}1400\text{ cm}^{-1}$  and the ring deformation at  $721\text{ cm}^{-1}$  [20],



Fig. 15. SEM of the cross-section of lithium polyborate fiber from Sol 3.

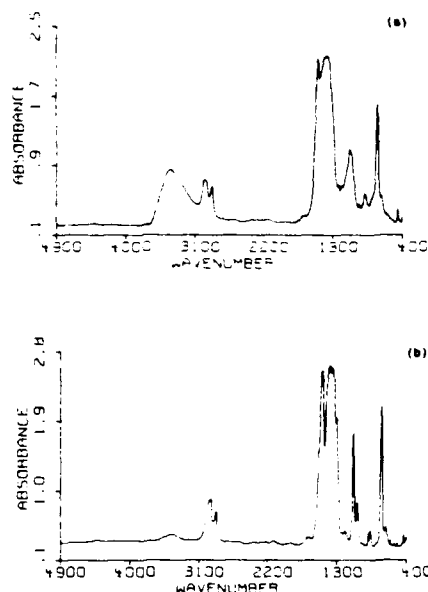


Fig. 16. IR spectra of (a) the sol derived from the partial hydrolysis and polycondensation of trimethoxyboroxine in presence of poly(ethylene oxide) and (b) trimethoxyboroxine.

indicating that the polyborate from the controlled hydrolysis process has a boroxine ring structural component. Thermogravimetric analyses of the viscous sol show weight losses of 15–25 wt% when held isothermally at temperatures ranging from 110 to  $190^{\circ}\text{C}$ . The calculated weight loss for dehydration of boric acid to boric oxide would be 44%. Considerably lower weight losses observed for the formation of boron oxide structures during the thermal analysis of the polyborate sol indicate that elimination of methanol presumably takes place from partially hydrolyzed polyborate structures such as (A) or (B) in figure 17, obtained from either a partial hydrolysis and polycondensation of trimethoxyboroxine, or from a polycondensation reaction between trimethoxyboroxine and boric acid resulting from the hydrolysis of some trimethoxyboroxine rings in an initial step [21]. A subsequent study revealed that spinnable, viscous sols could also be formed by the reaction of trimethoxyboroxine and boric acid in presence of high molecular weight poly(ethylene oxide) or poly(N-vinylpyrrolidinone) as a polymer additive. Studies related to continuous filament formation and thermal treatment, as well as morphological

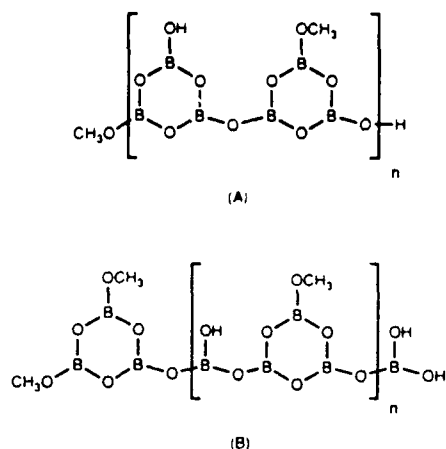


Fig. 17. Probable polyborate structures from the partial hydrolysis and polycondensation of trimethoxyboroxine.

aspects of the fibers derived through this route are in progress and will be reported in the future.

### 3.7. Attempted ammonium polyborate synthesis

Synthesis of spinnable sol-gel derived polyborates with ammonium counterion would be relevant in the context of providing a cation that can be removed during heat treatment as ammonia, resulting in the formation of a metal ion-free boron oxide precursor for chemical conversion to boron nitride fibers. However, the reaction between trimethoxyboroxine and aqueous ammonium hydroxide appeared to result in the formation of a trimethyl borate-ammonia adduct. The same adduct was also obtained by bubbling ammonia gas into trimethyl borate [22,23] in another experiment. This was also inferred from the identical IR spectra (not shown) obtained for the products isolated from the two reactions.

Synthesis of ammonium polyborate was also attempted by a metal-ammonium counterion exchange between a sodium polyborate sol obtained from trimethoxyboroxine (see section 2.5.) and ammonium bromide or ammonium iodide. Solubility related problems and a lack of evidence for exchange by a <sup>23</sup>Na NMR experiment made these preliminary studies inconclusive.

### 4. Concluding remarks

Lithium polyborate gels have been synthesized from both tri-*n*-butyl borate and trimethoxyboroxine. A study of molecular structure using multinuclear NMR and IR indicates mechanistic similarities in the two sol-gel processes. Presence of tricoordinate and tetracoordinate borons as well as the counterion environment can be conveniently examined by high resolution <sup>11</sup>B NMR and <sup>7</sup>Li NMR. Differential thermal analysis and X-ray diffraction studies indicate that a crystallized phase, approximating a mixed oxide phase of the composition of Li<sub>2</sub>O · 2B<sub>2</sub>O<sub>3</sub>, was obtained from the lithium polyborate gels heat treated to temperatures above 600 °C.

Fiber formation prior to gelation can be effected in polyborate sol-gel systems with the lithium counterion. The fibers dry quickly in air and the gel fibers obtained are brittle. The potential for improved spinnability of such sols by the addition of high molecular weight polymer processing aids such as poly(*N*-vinylpyrrolidinone) has been explored. Lithium polyborate fibers with porous microstructures have been obtained through sol-gel processes from tri-*n*-butyl borate as well as trimethoxyboroxine. A polyborate network with a porous microstructure and without a counterion is expected to be a suitable precursor for high performance materials such as boron nitride fibers. Since nitriding of boron oxide with ammonia is a diffusion controlled process [24], a porous boron oxide fiber structure from a sol-gel process may prove to be a suitable alternative to melt-extruded boron oxide fibers. However, whether the porous fiber structures can be deformed and consolidated during nitriding to produce dense, oriented boron nitride filaments remains to be explored.

Preliminary experiments reveal that controlled hydrolysis and polycondensation of trimethoxyboroxine lead to the formation of viscous sols. The partially hydrolyzed polyborate structure obtained in the reaction seems to fulfil the requirements of providing better yields of boron oxide upon heat treatment, eliminating undesirable metal counterions, as well as showing better processibility in the context of fiber formation. Spinnability of these

sols can be improved by the addition of poly(ethylene oxide) or poly(N-vinylpyrrolidinone) as a processing additive. IR and TGA results indicate that sol-gel derived precursors to a single-component boron oxide system can be obtained by the partial hydrolysis and polycondensation involving trimethoxyboroxine.

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## BORON NITRIDE FIBERS FROM POLYBORATES

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### Introduction

Conversion of polymer precursors to high performance boron nitride fibers is being explored through a fundamental study of the mutually dependent chemical and morphological requirements in precursor polymer synthesis, formation of continuous precursor fibers, and thermochemical conversion to oriented boron nitride fibers. The premise of this research is that the difficulty encountered by previous researchers [1]-[8] in obtaining complete conversion of boron oxide to boron nitride, especially at the core of melt spun boron oxide fibers, will be eliminated by using a porous borate gel precursor fiber. Gel fibers are also likely to be amenable to orienting deformation during nitridation. Experiments conducted in our laboratories have shown that borate gel precursor fibers can be spun from a sol produced from condensation of trimethoxyboroxine and boric acid in the presence of a low concentration of high molecular weight polymer, such as poly(ethylene oxide) or poly(N-vinylpyrrolidone) [9,10,11]. Requirements to be investigated here include reproducible synthesis of a precursor polymer, development of a continuous fiber formation process, and thermochemical conversion and consolidation to yield dense boron nitride fibers. The effect of imposed axial stress on the evolution of morphology will be studied in order to identify conditions that could lead to high axial orientation in the boron nitride fibers.

The close similarity in structure and mechanical properties between graphite and boron nitride suggests that the potential does exist to obtain high modulus boron nitride fiber by orienting the graphite-like, sheet crystallites of boron nitride.

### Experimental

**Synthesis.** 40 ml trimethoxyboroxine (0.2755 mole) was added by gas-tight syringe transfer to 6.021 g boric acid (0.0974 mole) and 1.000 g poly(N-vinylpyrrolidone) (PVP  $M_w = 360,000$ ). A 100 ml reaction flask with teflon boiling chips and a 100 ml receiving flask were used on a high boiling distilling apparatus (Ace Glass Model 6563). The reaction flask was immersed in an oil bath. Boiling began after the slurry was heated to 115°C under a slight vacuum (630 to 660 mm Hg). By heating to 120 - 125°C, a solution was obtained and distillate started to collect. The temperature of the vapor in the distillation column was 47°C. To maintain distillation, the bath temperature was increased gradually to 175°C over 40 minutes. 15.2 ml of distillate was generated in the process. The product was a deep yellow, viscous solution (Sol 1, 2.4 wt% PVP) at 175°C which, on cooling to room temperature, hardened to a tan solid.

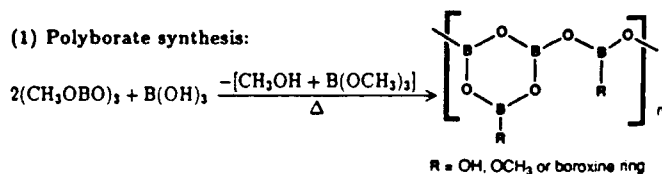
The procedure used to obtain Sol 1 was again repeated, except that it was scaled up four times and a 3:1 mole ratio of trimethoxyboroxine to boric acid was used. The reaction flask was heated to 192°C over 50 minutes, with a total of 68.8 ml of distillate collected. The product was a deep yellow, viscous solution (Sol 2, 2.4 wt% PVP) at 192°C which also hardened to a tan solid on cooling to room temperature. The majority of the product was poured directly into the small scale spinning apparatus (Figure 1) before it cooled.

Hand-drawn filaments of Sol 1 were nitrided with a constant flow of ammonia over an alumina boat. Samples were made separately by heating at a rate of 1°C/min to 200°C and held for 2 hours, 300°C and held for 30 minutes, 500°C and held for 30 minutes, and 700°C and held for 30 minutes. Each sample was cooled back to room temperature at about 2°C/min. Sol 2 was spun using an apparatus as shown in Figure 1. 200 psi nitrogen pressure was used to extrude the polyborate at 135°C through ten 63.5  $\mu$  diameter spinneret holes. A wind-up rate of  $\sim 13$  ft/min was used to spin these fibers. A 40  $\mu$  Mott filter was used to prevent clogging of the spinneret. Storage of fibers on a bobbin in a large dessicator is required in order to prevent hydrolysis prior to thermochemical conversion. The fiber diameters were measured by scanning electron microscopy to be 100  $\mu$ . A fiber sample was heated at a rate of 0.5°C/min to 200°C, held for 2 hours, and cooled to room temperature at about 2°C/min.

**Characterization.** FT-IR spectra of the product, Sol 1, boric acid and trimethoxyboroxine, as well as nitrided products were obtained (Figures 2 and 3). FT-IR spectra were obtained with Nicolet 60SX and Nicolet 520 systems. Sol 1 (re-melted at 170°C) and trimethoxyboroxine were each analyzed between AgCl plates. Boric acid and the nitrided products were analyzed as KBr pellets. X-ray diffraction patterns of hexagonal boron nitride powder from Aldrich Chemical Company, Sol 1, and nitrided products of Sol 1, were obtained with a Rigaku D/Max-B system operating at 45 kV and 100 mA (Figure 4). The radiation used was Ni-filtered Cu K $\alpha$  (wavelength 0.1542 nm). Melt viscosity and melt stability of Sol 2 were analyzed with a Rheometrics Dynamic Spectrometer using 25 mm diameter plates, 1 mm gap, 1% strain, and 1 rad/sec oscillation at 150°C.

### Results and Discussion

The mole ratio of trimethoxyboroxine to boric acid was purposely not 1:1 at the start of the polycondensation reaction for Sol 1 and Sol 2. Because of trimethyl borate-methanol azeotrope formation and concurrent hydrolysis of trimethoxyboroxine with polycondensation, reactions with a 1:1 stoichiometry of trimethoxyboroxine to boric acid on cooling result in precipitation of boric acid [11]. Stoichiometries of 2:1 and greater have therefore been employed. The infrared spectrum of Sol 1 shows a blending of the spectral features of trimethoxyboroxine and of boric acid (Figure 1) [12,13]. A decrease in the C-O stretch at 1080  $\text{cm}^{-1}$  and retention of the ring deformation at 720  $\text{cm}^{-1}$  are representative of the proposed polyborate structure, Equation 1 [11]. The remaining broad hydroxyl band, 3200-3500  $\text{cm}^{-1}$ , for Sol 1 is indicative of incomplete condensation.



Hand-drawn filaments from Sol 1 were batch nitrided in an ammonia atmosphere at a heating rate of 1°C/min to 200, 300, 500, and 700°C. Infrared spectra of the samples indicate that there is a loss of hydroxyl by 200°C and evidence of a partially nitrided structure. Infrared spectra for samples exposed to higher nitriding temperatures show increased absorbances for the N-H stretch at 3430  $\text{cm}^{-1}$ , the B-N stretch at 1350  $\text{cm}^{-1}$ , and the B-N-B bending at  $\sim 800$   $\text{cm}^{-1}$ . The

grey color of the 700°C nitrided sample and the presence of an 1100  $\text{cm}^{-1}$  band is indicative of the B-C asymmetric stretch of some boron carbide present [14]. The boron carbide is expected to be removed with further nitriding. X-ray diffraction patterns (Figure 4) show the development of a turbostratic-like boron nitride pattern in the 700°C nitrided sample from the initially amorphous polyborate [15].

An initial dynamic viscosity for Sol 2 of 5000 Poise at 150°C, increasing to about 7000 Poise over a period of one hour, was measured. With loss of the azeotrope, the viscosity is expected to increase. Continuous melt spinning was possible at 135°C, 200 psi nitrogen using a ten hole spinneret with 63.5  $\mu$  holes. However, only large diameter, 100  $\mu$ , fibers were spun because of fiber breakage at higher wind-up rates. Heating the fibers at 0.5°C/min to 200°C produced some beads on the fibers. There is a total loss of shape of the filaments by 300°C. Probably a lower temperature soak will help stabilize the fiber shape. Ideally ~10  $\mu$  diameter fibers are desired for nitriding [8].

For spinning polyborate, a heated tube can be used to extend the molten region for drawing the fibers. Other stoichiometries such as a 4:1 mole ratio of trimethoxyboroxine to boric acid can be used in order to lower the melt viscosity to about 1000 Poise at the spinneret. It may also be possible to ammoniate the polyborate system with urea prior to spinning to decrease nitriding time during subsequent thermochemical conversion. These and related aspects are currently being explored and will be discussed.

## Acknowledgement

The research reported here was supported by the Georgia Tech Polymer Education and Research Center and the Office of Naval Research, Polymer Chemistry Division.

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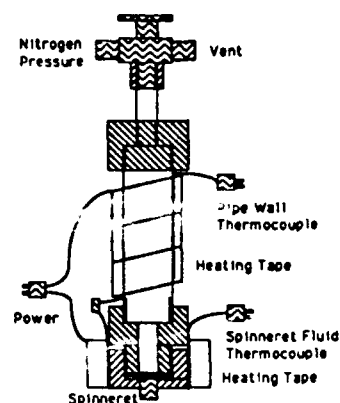


Figure 1. Schematic of experimental apparatus for melt spinning.

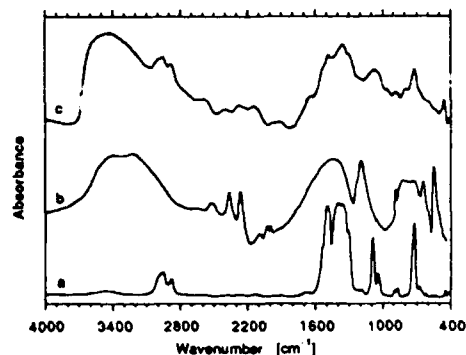


Figure 2. Infrared spectra of a) trimethoxyboroxine, b) boric acid, and c) Sol 1.

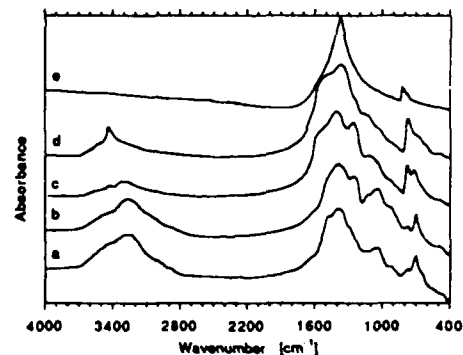


Figure 3. Infrared spectra of Sol 1 nitrided to a) 200°C, b) 300°C, c) 500°C, and d) 700°C. e) Reference BN (Aldrich Chemical Company).

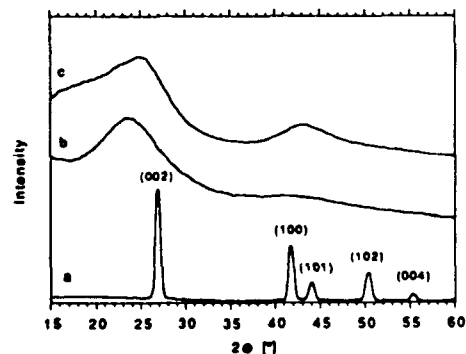


Figure 4. X-ray diffraction patterns of a) hexagonal BN (Aldrich Chemical Company), b) Sol 1 (amorphous), and c) Sol 1 after nitriding to 700°C (turbostratic).

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# SYNTHESIS OF FIBER FORMING POLYBORATES

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## Introduction

A method for the preparation of boron nitride fiber from melt spun boron oxide fiber was reported by Economy, *et al.*, as a result of research efforts at The Carborundum Company [1]-[6]. Boron nitride fibers were prepared by allowing the boron oxide precursor fibers to react with ammonia under conditions of controlled heating from room temperature to  $\sim 800^\circ\text{C}$ , followed by a final stabilization for 5-10 seconds under tension at  $\sim 2000^\circ\text{C}$  in a nitrogen atmosphere. Fibers with a tensile strength of  $300 \times 10^3$  psi (2.0 GPa) and a tensile modulus of  $50 \times 10^6$  psi (350 GPa) were produced. The process was hampered by the slow diffusion of ammonia into the melt spun boron oxide fiber, causing the heating schedule to last up to 14 hours in some cases.

Sol-gel routes to porous polyborate fibers have been demonstrated in research conducted in our laboratories [7,8]. Polycondensation of trimethoxyboroxine and boric acid to produce spinnable polyborate formulations is discussed here. The premise here is that the difficulty encountered by Economy in obtaining complete conversion of boron oxide to boron nitride, especially at the core of melt spun boron oxide fiber, would be eliminated by using a porous borate gel precursor fiber.

Various routes to polyborates have been reported in the literature. One of these routes involves the reaction of cyclohexanol with boric acid or boron oxide with removal of water as an azeotrope with toluene or xylene [9,10]. Polyborates have also been prepared by hydrolysis and polycondensation involving boron alkoxides in the presence of alkali metal alkoxides whereby metals become counterions to tetra-coordinate boron in the polyborate structure [11]-[14]. Concern over the presence of residual organics, such as toluene or xylene which may lead to excessive carbon during thermochemical conversion, or alternatively tetra-coordinate metal ions, which may be difficult to remove from polyborate precursors, has motivated the development of a more direct polycondensation of trimethoxyboroxine and boric acid to form a polyborate. Spinnable polyborate precursors to boron nitride are formed with a low concentration of a high molecular weight polymer as a rheological aid which is fugitive during thermochemical conversion.

## Experimental

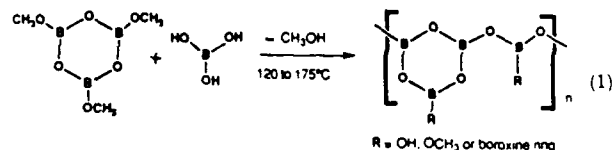
**Synthesis.** 40 ml trimethoxyboroxine (0.2755 mole) was added by gas-tight syringe transfer to 6.021 gm boric acid (0.0974 mole) and 1.000 gm poly(ethylene oxide) (PEO  $\bar{M}_n = 100,000$ ). A 100 ml reaction flask with teflon boiling chips and a 100 ml receiving flask were used on a high boiling distilling apparatus (Ace Glass Model 6563). The reaction flask was immersed in an oil bath. Boiling began after the slurry was heated to  $115^\circ\text{C}$  under a slight vacuum (630 to 660 mm Hg). By heating to  $120 - 125^\circ\text{C}$ , a solution was obtained and a distillate started to collect. The temperature of the vapor in the distillation column was  $47^\circ\text{C}$ . To maintain distillation, the bath temperature was increased gradually to  $150^\circ\text{C}$  over 50 minutes. 10.4 ml of distillate was generated in the process. A translucent, light yellow, viscous product solution (Sol 1, 2.2 wt% PEO) was obtained after cooling to room temperature.

The procedure to obtaining Sol 1 was again repeated, except that 1.000 gm of poly(N-vinylpyrrolidone) (PVP  $\bar{M}_n = 360,000$ ) was substituted for PEO. The reaction flask was heated to  $175^\circ\text{C}$  over 40 minutes with a total of 15.2 ml of distillate collected. The product was a deep yellow, viscous solution (Sol 2, 2.4 wt% PVP) at  $175^\circ\text{C}$  which, on cooling to room temperature, hardened to a tan solid.

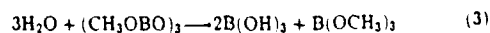
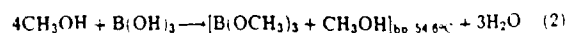
**Characterization.**  $^{13}\text{C}$  NMR spectra of trimethoxyboroxine, methanol, trimethyl borate, Sol 1, and the distillates were obtained using a Varian XL-400 NMR spectrometer. The resonances were externally referenced with TMS in  $\text{CDCl}_3$  to 0.0 ppm using coaxial 5 mm (sample, flame-sealed) and 10 mm (lock compound and reference) glass tubes. FT-IR spectra of the products, Sol 1 and Sol 2, as well as the aforementioned compounds were obtained. FT-IR spectra were obtained with a Nicolet 60SX system. The liquids were analyzed between AgCl plates, whereas the solid, boric acid, was analyzed as a KBr pellet. A sample from Sol 2 was re-melted at  $170^\circ\text{C}$  between the AgCl plates to form a thin film for analysis. Thermogravimetric analysis (TGA) scans were obtained for the PEO, PVP, boric acid, and the product sols using a Perkin-Elmer TGA Series 7 at a heating rate of  $5^\circ\text{C}/\text{min}$  to  $250^\circ\text{C}$  in dry air. The melting temperature of Sol 2 was found by differential thermal analysis (DTA) with a Mettler TA2000.

## Results and Discussion

In the limiting case of a balanced trifunctional polycondensation of trimethoxyboroxine and boric acid, there will be a simultaneous presence of sol (soluble polymer) and gel (insoluble polymer) after gelation. Highly branched species will preferentially be converted to the gelled network as the reaction continues beyond the gel point [15].



The molar ratio of trimethoxyboroxine to boric acid was purposely not balanced at the start of the polycondensation reaction for Sol 1 and Sol 2. Reactions with a 1:1 stoichiometry result in precipitation of boric acid on cooling to room temperature.  $^{13}\text{C}$  NMR of the distillates showed a nearly 1:1 molar azeotrope of trimethyl borate and methanol. A nearly 1:1 trimethyl borate and methanol azeotrope at  $54.6^\circ\text{C}$ , 760 mm Hg has been reported [16]. This azeotrope is known to be formed by the reaction of methanol and boric acid to produce trimethyl borate and water (Equation 2) [10]. It is inferred from the azeotrope formation that the methanol produced during condensation reacts with boric acid under the reaction conditions to produce trimethyl borate and water. Without removal of water in the reaction, as much as twice the amount of lost boric acid may be regenerated by partial hydrolysis of trimethoxyboroxine (Equation 3) [17]. It is estimated that due to azeotrope formation and concurrent hydrolysis of trimethoxyboroxine, the polycondensation must be started at about a 2:1 or larger ratio of trimethoxyboroxine to boric acid.





The infrared spectra of Sols 1 and 2 show a blending of the spectral features of trimethoxyboroxine and of boric acid (Figure 1) [18,19]. A decrease in the C-O stretch at  $1080\text{ cm}^{-1}$  and the retention of the ring deformation at  $720\text{ cm}^{-1}$  are representative of the proposed polyborate structure, Equation 1. Sol 2 shows a noticeable reduction in the C-H stretch bands,  $2950$  and  $2880\text{ cm}^{-1}$ , relative to Sol 1. This is most likely due to further condensation with more of the methanol-trimethyl borate azeotrope being removed at the higher reaction temperature. The remaining broad hydroxyl band,  $3200\text{--}3500\text{ cm}^{-1}$ , for Sols 1 and 2 is indicative of incomplete condensation.

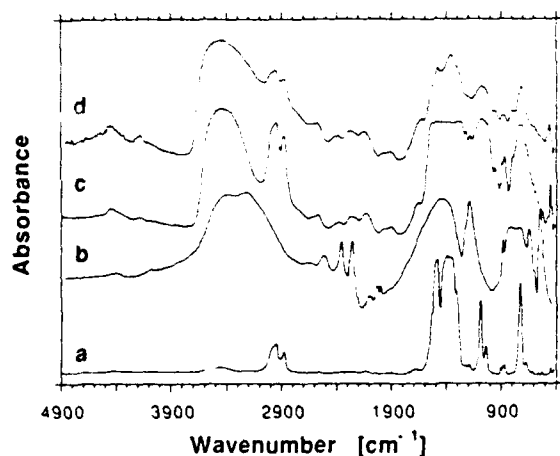


Figure 1. Infrared spectra of a) trimethoxyboroxine, b) boric acid, c) Sol 1, and d) Sol 2.

Methyl polyborate begins to decompose in air at about  $165^{\circ}\text{C}$  which is  $35^{\circ}\text{C}$  above the decomposition temperature (boiling point) of trimethoxyboroxine [10]. It is predicted that polyborates are more thermally stable than the corresponding metaborates since they are closer to boron oxide, a highly thermally stable species, in the continuum  $(\text{RO})_3\text{B} \dots (\text{ROBO})_3 \dots (\text{ROBO})_6\text{B}_2\text{O}_3 \dots \text{B}_2\text{O}_3$  [10]. TGA of Sols 1 and 2 heated to  $250^{\circ}\text{C}$  to carry out thermochemical conversion results in about a 25% weight loss.

A unique result is found when PVP is added to polyborate. With just 2.4 wt% PVP, the resulting product is a solid which can be re-melted by heating above  $115^{\circ}\text{C}$  (Sol 2), whereas the polymerization performed in the same manner with 2.2 wt% PEO is a viscous solution at room temperature (Sol 1). This difference may be a result of dative bonding by PVP with polyborate (Figure 2). In earlier studies [7,8], an additional resonance in the tetracoordinate boron region was observed by  $^{11}\text{B}$  NMR when 1-methyl-2-pyrrolidinone was added to the polyborate sol or trimethoxyboroxine. The polycondensation of trimethoxyboroxine and boric acid necessitates heating from  $120^{\circ}\text{C}$  to  $175^{\circ}\text{C}$  for reaction and azeotropic removal of trimethyl borate and methanol from the viscous sol. This allows, by reheating, the formation of a fluid containing the polyborate and the respective polymer processing aid, if loss of the methanol-trimethyl borate azeotrope is prevented.

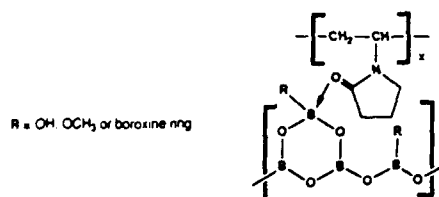


Figure 2. Possible structure of polyborate in the presence of PVP.

Since the Sol 2 precursor can be re-melted and solidified, the requisite viscosity for fiber spinning can be attained by heating, and the rigidity necessary for maintenance of fiber shape can be attained by cooling. Fibers from polyborate with PVP (Sol 2) were found to be much more hydrolytically stable than those with PEO (Sol 1). With further removal of the azeotrope from the polyborate fiber, its  $T_m$  would be expected to increase. A favorable implication of thermoplasticity is that the fibers may be deformed during thermochemical conversion in ammonia to yield an oriented boron nitride morphology.

## Acknowledgement

The research reported here was supported by the Georgia Tech Polymer Education and Research Center and the Office of Naval Research, Polymer Chemistry Division.

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# POLYMERIC MATERIALS SCIENCE AND ENGINEERING



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# SYNTHESIS AND CHARACTERIZATION OF SPINNABLE SOL-GEL DERIVED POLYBORATES

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## Introduction

In recent years, considerable progress has been made in low temperature synthesis of glasses and ceramics through the sol-gel route involving the hydrolysis and polycondensation of metal alkoxide solutions. Gel fibers drawn in the sol-gel process from viscous alkoxide solutions serve as precursor materials for oxide glass fibers since they can be converted into oxide fibers on consolidation [1]. It is important to identify the composition of the metal alkoxide solutions which become spinnable in the course of hydrolysis and condensation [2]. Fibers of the systems  $\text{SiO}_2$ ,  $\text{SiO}_2 - \text{Al}_2\text{O}_3$ ,  $\text{SiO}_2 - \text{TiO}_2$ ,  $\text{SiO}_2 - \text{ZrO}_2$ , and  $\text{ZrO}_2$  have been prepared by this route [1,3].

Unlike silicon alkoxides, boron alkoxides hydrolyse rapidly to form boric acid which makes the usual hydrolysis-polycondensation sol-gel route unsuitable for the formation of polyborate gels [4]. Recent studies by Weinberg *et al.* [4] and Brinker *et al.* [5,6,7] have demonstrated that the borate gels can be formed by the reaction of trialkylborates with lithium methoxide in mixed alcohol/water solvents. The proposed mechanism for gelation in the organoborate system is shown in Scheme 1 [5]. The tendency to form the trimeric ring containing both trigonal and tetrahedral boron atoms and the stability of the tetrahedral boron with respect to hydrolysis serve as the important criteria for the formation of aqueous polyborates [8]. This investigation involves studies related to the molecular structure development as well as fiber formation in the borate sol-gel system.

## Experimental

**Synthesis.** The procedure is similar to the one reported by Weinberg *et al.* [4]. Lithium methoxide (0.066 mole) was dissolved in methanol (0.616 mole) and freshly distilled water (0.14 mole). Tri-*n*-butylborate was added dropwise to the above solution. After stirring at room temperature, the clear sol was aged at 50°C in a 95% relative humidity environment. Fibers could be drawn from the viscous translucent sol after 12 hours (Sol 1). Part of Sol 1 was dried at 90°C in vacuum for 12 hours to obtain a white powder. When a sol of the same initial composition was aged at room temperature in 100% relative humidity, gelation occurred typically in 18-20 hours (Sol 2). The sol-gel reaction was also carried out using trimethoxyboroxine (0.094 mole) and lithium methoxide (0.085 mole) in methanol and aging the mixture at room temperature in a 100% relative humidity environment (Sol 3).

**Characterization.**  $^{11}\text{B}$  NMR spectra of the reaction mixtures were obtained using a Varian XL-400 NMR spectrometer operating at 128.311 MHz. When possible, quartz NMR tubes were used to minimize the broad boron glass background. The resonances were externally referenced to sodium borohydride (-42.0 ppm with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  defined as 0.0 ppm).  $^7\text{Li}$  NMR spectra were obtained at an operating frequency of 155.454 MHz using LiBr in a tetraglyme/acetone- $\text{d}_6$  mixed solvent system as external standard. The viscous polyborate Sol 1 was dissolved in 1-methyl-2-pyrrolidinone (NMP) and the  $^{11}\text{B}$  NMR spectrum of this solution was also obtained. FT-IR (KBr disc) of the polyborate fibers as well as that of the gel were obtained using a Nicolet 60SX system. Thermogravimetric analysis (TGA) scans were obtained using a Perkin-Elmer TGA7 system.

## Results and Discussion

**Sol-gel process with tri-*n*-butyl borate.** A 50% solution of the viscous, fiber-forming sol (Sol 1) in NMP was used for both  $^{11}\text{B}$  and  $^7\text{Li}$  NMR studies since hydroxylic solvents, such as methanol, were found to alter the polyborate structure drastically. Figure 1 shows the presence of a boron resonance at 18.5 ppm due to borons in trigonal environment and also resonances at high field (2.9 and 2.0 ppm) due to tetrahedral borons (Scheme 1) in the borate structure. The latter resonances are temperature-dependent with a complete disappearance

of the 2.9 ppm resonance with an increase in temperature to 80°C which is reversible with a decrease back to 20°C. More experiments are planned to elucidate this observation.  $^7\text{Li}$  NMR of Sol 1 (Figure 2) showed two main resonances at -0.05 ppm and 0.16 ppm due to the lithium counterion in the tetrahedral boron environment and lithium in LiOH due to hydrolysis of LiOMe. Presumably, some of the LiOMe remains unreacted in the initial equilibrium leading to the formation of tetrahedral borons [5]. The structure development as monitored by  $^{11}\text{B}$  NMR (without NMP in the samples) indicated that for Sol 2 with the same initial composition as Sol 1 and aged at room temperature, the tetracoordinate boron appears at 1.8 ppm and the tricoordinate boron appears at 18.5 ppm. In the corresponding  $^7\text{Li}$  NMR spectrum, the lithium counterion resonance appears at -0.05 ppm. A resonance assigned to LiOH also appears at 0.16 ppm.

Sol-gel reaction with trimethoxyboroxine. The mechanistic validity of Scheme 1 was clearly borne out by studies with trimethoxyboroxine. Complexation with LiOMe to form tetrahedral borons followed by hydrolysis-condensation in a humid atmosphere results in the formation of the lithium polyborate gel. In the  $^{11}\text{B}$  NMR spectrum of Sol 3 (without NMP) the tetracoordinate boron appears at 1.8 ppm and the tricoordinate boron appears at 12.8 ppm. In the corresponding  $^7\text{Li}$  NMR spectrum, the lithium counterion resonance appears at -0.13 ppm. There was no LiOH resonance observed. The FTIR spectra (Figure 3) of the Sol 1 borate fiber as well as the gel from trimethoxyboroxine Sol 3 show the presence of the B-O stretch associated with a tricoordinate boron unit ( $1360\text{ cm}^{-1}$ ) and the presence of tetracoordinate borons ( $1025\text{ cm}^{-1}$ ).

Thermogravimetric analysis. The TGA profile of the gel (from tri-n-butyl borate reaction) in air shows a weight loss of 20% which is nearly complete at 400°C. No black residue due to organics was obtained when the sample was heat treated isothermally at 900°C for 4 hours.

SEM of the polyborate fiber. SEM examination of both the cross-section and the surface of the fiber indicated a highly porous structure.

**Summary.** The results discussed indicate that fiber formation is possible in polymer borate sol-gel systems prior to gelation and that polymer growth leading to the borate gel is found to occur in the case of trimethoxyboroxine (Sol 3). Work involving a study of the borate sol-gel process incorporating different counterions will also be presented at the conference.

## Acknowledgement

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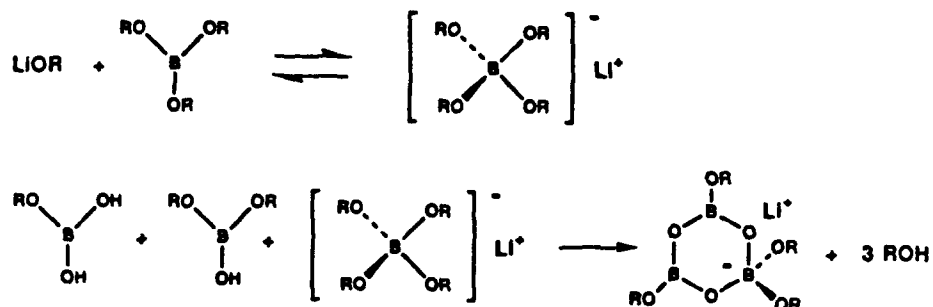
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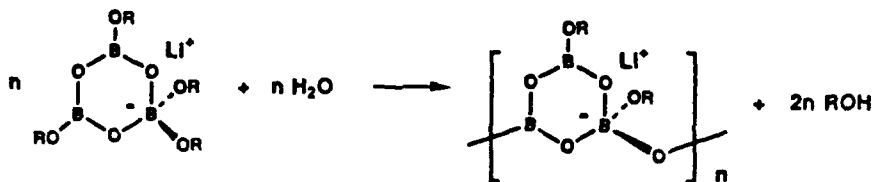
(i) Partial hydrolysis of borate precursor:



(ii) Condensation to form small primary units:



(iii) Linkage of units to form polymer network:



Scheme 1. Lithium polyborate sol-gel reaction steps proposed by Brinker, *et al.* [5].

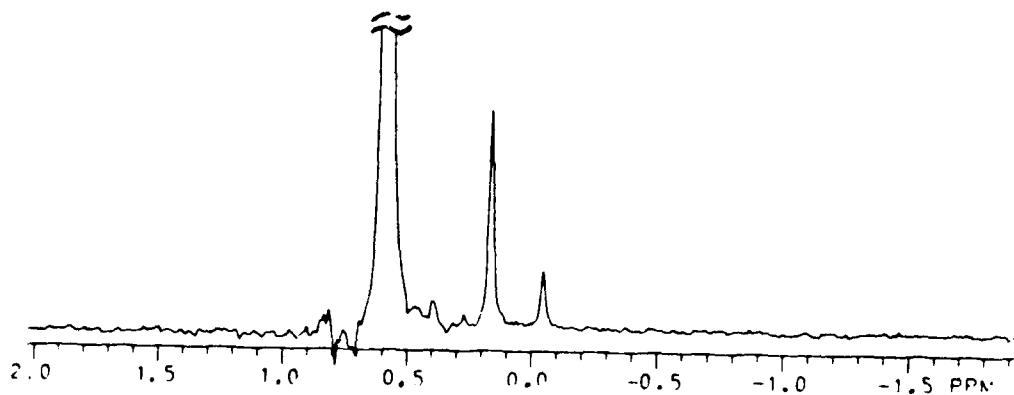


Figure 2.  $^7\text{Li}$  NMR spectrum of Sol 1 (50% in NMP) at 20°C with an external reference of 2 ml 0.85M LiBr in tetraglyme plus 1 ml acetone- $\text{d}_6$  (0.60 ppm relative to 0.5M LiCl in  $\text{D}_2\text{O}$  defined as 0.0 ppm).

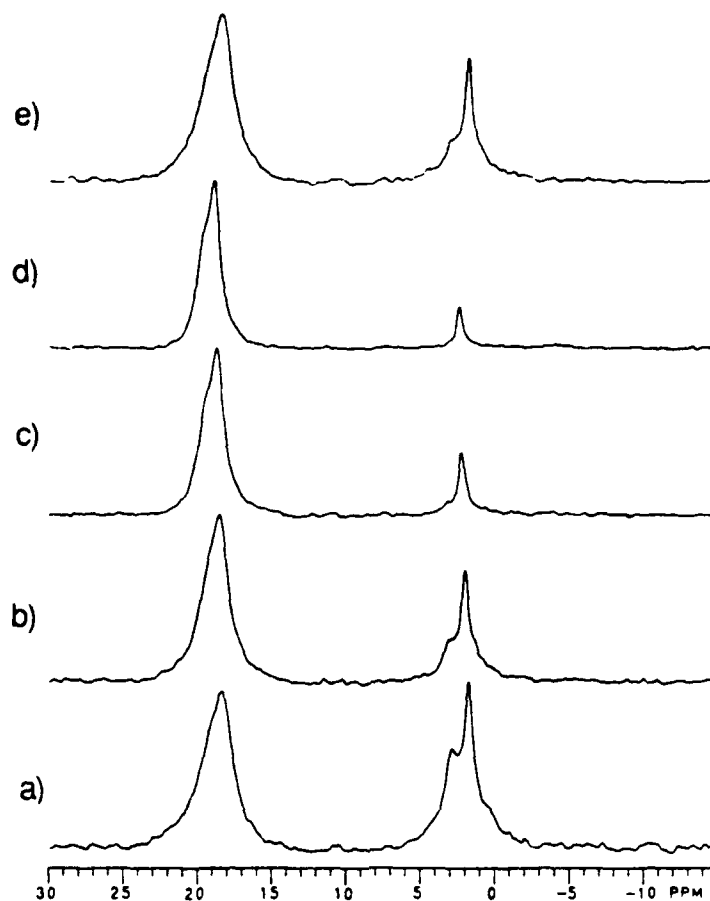


Figure 1.  $^{11}\text{B}$  NMR spectra of Sol 1 (50% in NMP) at different temperatures: a) 20°C b) 40°C c) 60°C d) 80°C e) cooled back to 20°C. An external reference of 0.25M  $\text{NaBH}_4$  in tetraglyme at -41.0 ppm was used.

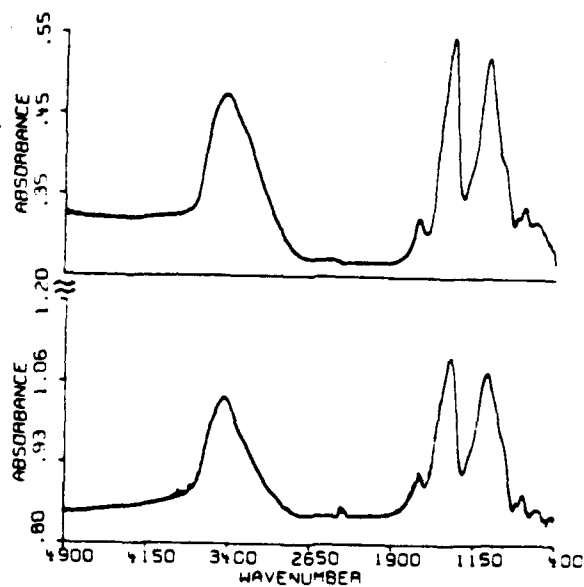


Figure 3. FT-IR spectra (KBr disc) of dried lithium polyborate fiber (Sol 1, top) and dried gel from trimethoxyboroxine (Sol 3, bottom).



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